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THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED TEMPERATURE ON CO--ETC(U)

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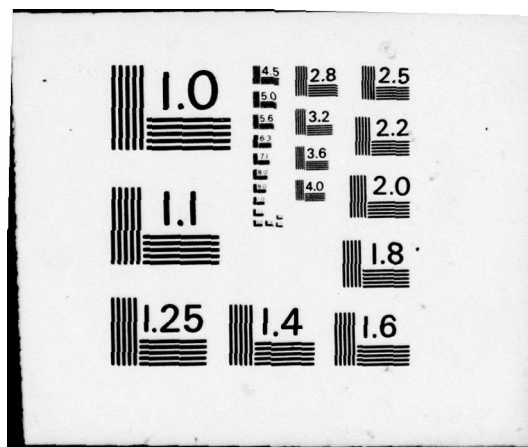
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THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED
TEMPERATURE ON COMPOSITE STRUCTURES

CO-EDITED BY

J. R. VINSON

R. B. PIPES

W. J. WALKER

D. R. ULRICH

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College of Engineering

University of Delaware

Newark, Delaware

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AFOSR SCIENTIFIC REPORT

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THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED
TEMPERATURE ON COMPOSITE STRUCTURES

Co-Edited by

J.R. Vinson

R.B. Pipes

W.J. Walker

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CENTER FOR COMPOSITE MATERIALS

UNIVERSITY OF DELAWARE *univ, Newark*

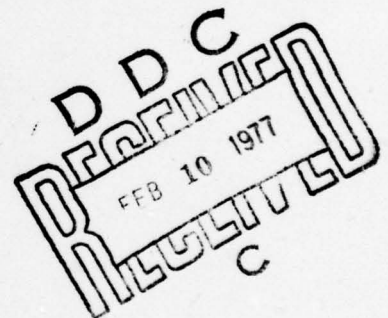
March 30 - 31, 1976

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UNITED STATES AIR FORCE

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and Mechanics research dealing with the effects of relative humidity and elevated temperature on composite structures. In addition, pacing research topics were identified which must be addressed in the future if the goal of aerospace structural applications with advanced composites is to be achieved.

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TRANSACTIONS OF THE
WORKSHOP
ON

THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED
TEMPERATURE ON COMPOSITE STRUCTURES

Sponsored by the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

and the

CENTER FOR COMPOSITE MATERIALS
UNIVERSITY OF DELAWARE

March 30 - 31, 1976

Co-Edited By

J.R. Vinson
R.B. Pipes
W.J. Walker
D.R. Ulrich

ABSTRACT

Understanding the influence of combined relative humidity and elevated temperature on the performance of advanced polymer matrix composite structures is a matter of pacing importance to the Air Force in the development of future innovative structures. Degradation of structural strength and durability must be predictable if advanced composites are to be widely accepted as an alternate material in aerospace structural design. These Transactions are the result of a Workshop which discussed the state-of-the-art in both Polymer Chemistry and Mechanics research dealing with the effects of relative humidity and elevated temperature on composite structures. In addition, pacing research topics were identified which must be addressed in the future if the goal of aerospace structural applications with advanced composites is to be achieved.

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INTRODUCTION

This report contains an edited transcription of the Workshop on "The Effects of Relative Humidity and Elevated Temperature on Composite Structures." The format selected is therefore of a dialogue nature as it occurred at the Workshop. This has the advantage of conveying to the reader a sense of the real time conduct of the meeting and the participant's interest.

Organization of the Workshop embodied the following major topics:

- a. Air Force and Industrial perspective of the Workshop topic (Report Section B).
- b. Review of previous technology in the Workshop topic area (Report Section C).
- c. Division of the Workshop topic area into five pre-selected categories with dual presentations in each subject. Presentations were given in each topic in order to reflect the interests and perceptions of a Polymer Chemistry (materials) approach and of a Structures (mechanics) approach to the subject (Report Section D).
- d. Finally, attendees were organized into discussion groups in each category area, with the objective of identifying pacing research areas. Results of these individual discussions were then presented to

all participants by selected discussion leaders
(Report Section F).

In most instances visual aid material has been included in this report. However, in several cases the reader will find that visual aids used by the speakers were not available for release at this time. The editors wish to apologize for this but in view of the interest expressed in the meeting we have elected to proceed with the report publication without further delay. In those sections where this has occurred the reader should contact the speaker directly for any needed clarification.

OPENING AND WELCOME

1

DR. VINSON: Good morning, ladies and gentlemen. We will now open our conference on The Effects of Relative Humidity and Elevated Temperatures on Composite Materials. And to welcome you, we have this morning Dr. E. Arthur Trabant, the President of The University of Delaware, and I must say that we are very fortunate in having Dr. Trabant as President here. He has a Ph.D. in applied mathematics from Cal. Tech. Later, he was the Chairman of Engineering Sciences at Purdue University. From 1960 to '66 he was Dean of Engineering at Buffalo, and from '66 to '68 Provost and Vice President for Academic Affairs at Georgia Tech.

In that year we were very fortunate in attracting him here to the University of Delaware, and I must say it is very nice to have a President who is an engineer and understands the problems of engineering, its jargon and its terminology.

Since that time our College of Engineering has flourished very well under his guidance and leadership. So, it is with a great deal of pleasure that I present to you Art Trabant.

DR. TRABANT: Thank you, Jack. After all of that I think I should smile at least.

Well, it is a pleasure to be here this morning, believe me, to welcome you to our university, The University of Delaware. And this is an important conference. Jack has mentioned the title, and you know it well, so there is no

need of repeating it.

There are three points that I am going to talk about. They are short, but in my mind they are important. Three independent events, three independent things, that I think come together and have caused this meeting to occur today at this particular university at this particular time. I want to go over those.

Now, the first point is that it was about two years ago that some faculty members in our College of Engineering - these were faculty members engaged in teaching and research in the field of composite materials, believed that there could be greater and there could be more rapid advances made if individuals who might be working in the field could form into and would form into research teams.

It was believed, too, that by bringing together those interested in this field there would be greater opportunities to develop courses, seminars, workshops in this new field.

So it was out of these desires that the College of Engineering Center for Composite Materials was conceived, developed, and finally approved by the faculty and all the way through, of course, to the Board of Trustees. Now, that was the first independent event.

Completely apart from that and preceding that decision in The College of Engineering, I mention the deep commitment of our University to continuing education. This facility that we are meeting in this morning, we call it splendid;

its real name is John M. Clayton Hall; it is a material, it is a tangible expression of our University's commitment to what we term "continuing education".

If you are new to our campus you may not be aware that although our University ranks 36th in enrollment in the land grant system, we ranked 8th among the nation's land grant colleges and universities in the number of opportunities for continuing education that our University affords the citizens of the State and Region.

So, on a per capita basis the University's continuing education effort ranks number one in the country. This means, of course, that the citizens of Delaware in particular have more opportunities for self-improvement on a part-time basis than do the citizens of any other state in the nation.

The third point, I'd like to bring to your attention is the following. It is that which has made this workshop a reality. I refer to the close working relationship that has existed between government, industry, and faculty, particularly in the sciences, since World War II. Now, higher education may truly be something of an ivory tower in some disciplines, in some academic fields, but certainly this is not true in the sciences and in engineering. And to my mind it is this close affiliation and mutual respect that was probably the real prompter for the Office of Scientific Research of the U.S. Air Force to sponsor this particular workshop.

So now I hope you understand what I have been trying to say, that it's not just chance that has brought us together today, but three independent elements that have made it possible for those attending this workshop to further their technical knowledge and skills.

Now, to me, each of these developments characterized the best features of American higher education and should indicate why it has been and should be the most widely supported in its endeavors of any other national enterprise in our country.

So now best wishes to all of you for an enjoyable stay at our University and a profitable and learning experience in the workshop.

Thank you very much.

DR. VINSON: Thank you very much, Dr. Trabant.

DR. TRABANT: A pleasure, thank you.

DR. VINSON: To start our first session, our session chairman is Dr. R. Byron Pipes. Every university needs new blood, bringing in new people, and particularly with a solid mechanics group that is primarily analytical, to bring in an experimental solid mechanician is truly a good addition. I'd say we were very fortunate to attract Dr. Pipes here a couple of years ago where he has become a very fine leader in our academic and research programs.

DR. PIPES: Thank you, Jack. I'd like to start this morning's first session by again welcoming you. We are indeed pleased that you could come. I think that it's obvious that the right and the important people are here today to attack the problem, and I think that we have the tools, we have the personnel, now we have the time, let's proceed to do it.

I'd like to take this opportunity to introduce Mr. William J. Walker of the Air Force Office of Scientific Research. Bill was first at the Jet Propulsion Laboratory, then at Boeing-Seattle in the Aerospace group prior to joining the Air Force Office of Scientific Research in 1972. He has endeavored to generate a strong program in the sciences which are of interest to the Air Force in pursuing their programs. I'd, therefore, like to turn the floor over to Bill, and Bill will present the objectives of the workshop at this time.

A. OBJECTIVES OF THE WORKSHOP

MR. WALKER: Thank you very much, Dr. Pipes. Before I start with the objectives here, I'd like to thank the people at the University of Delaware for hosting this conference, and very much thank you, the attendees, for the fine showing that we have here. This conference is sponsored by two groups within AFOSR, and I have a couple of my colleagues here I'd like to introduce at this time. The conference is jointly sponsored by the Directorate of Chemical Sciences and the Director of that Directorate is

here with us today, Dr. Don Ball--

Don, would you stand up, please?

Also, from Chemical Sciences, my colleague, Dr. Don Ulrich is also here.

The other group, the one that I'm associated with at OSR, is the Aerospace Sciences Directorate.

Without further ado, I'd like to move on, so if I could have the first view graph (W-1)?

When we started to put this Workshop together we recognized the need for discussion of the technical issue, but there was a deeper need, and so we start off with one of the objectives, to promote the interaction between the two communities, the materials and structures in this case, the polymer scientists and the structural mechanicians. And the second is identifying the research opportunities specifically related to the Workshop topic, both the polymer science and the structural mechanician inter-disciplinary research programs.

To accomplish that, the organizational committee, if you will, says, "How is the best way to do this?"

To promote the interaction, we cut it in this way (W-2) between the industrial and research communities and also the government that is involved in the composites problem, and also split the polymer science and the structural mechanics area, trying to promote here a representative group from each one of these communities.

Specifically, (W-3) we are interested in the degradation

WORKSHOP OBJECTIVES

1. Promote the interaction between two communities involved with composite materials and their application to structures
Polymer Science
Structural Mechanics
2. Identify research opportunities specifically related to workshop topic in both polymer science and structural mechanics and also interdisciplinary research

W-1

ACCOMPLISHMENT OF OBJECTIVES

	Industry	Research	Government
Polymer Science			
Structural Mechanics			

W-2

QUESTION FOR DISCUSSION

Degradation of composites due to environmental effects:
Combined moisture and temperature effects and other environments.

Degradation in terms of mechanical characteristics from both a materials and structures viewpoint.

W-3

of composites due to environmental effects, moisture and temperature and, as I am sure Dr. Thomas will talk about later, some other environmental considerations.

I think it's important to focus on the semantics of what we mean by degradation in terms of the mechanical characteristics from both a materials and structures point of view. Within that framework, what are we looking for from this Workshop? We look for the identification (W-4) of the mechanisms and parameters that govern the degradation processes, both in near term framework and the long range requirement sense, and being ever aware of the possibilities for new potentials coming out of independently driven research activities.

In terms of the Air Force applications (W-5) that we are looking at, we have the primary structural considerations, you also have the application of composites going into engine blades and static structures, and you have it being used in tactical missiles and strategic missiles, and also in the spacecraft business.

The environments that we run into for focusing on the research problem are entirely different from a systems point of view. So, while there is major emphasis currently from the Air Force in the airframe business, from the research point of view you must be cognizant of the other applications and the specifics of the environments that are concerned, so that we don't have any research gaps leading to deficiencies in our technology base theory.

WHAT ARE WE LOOKING FOR

Identification of mechanisms and parameters that govern these properties considering air force near term and long range requirements and new potentialities.

W-4

AIR FORCE APPLICATIONS

Airframe Primary Structure
Engine Blades and Static Structure
Tactical and Strategic Missiles
Spacecraft

W-5

The Workshop has been organized into discussion areas as shown here, (W-6) and we believe these are representative of what we see as the problem areas that can fit within these categories that you can discuss within two days.

And, finally, what do we anticipate for a workshop output (W-7)? The identification of the research goals, that is, the apparent research approaches that the research programs should pursue, and again, not so apparent research programs.

Always be aware of the good idea that somebody in the back room can "gin" up.

Within that framework, we are also looking for what the research emphasis ought to be again in the cooperative area of activity between polymer scientists, the mechanic approach, and interdisciplinary approaches. The identification of the needs and opportunities to match up with the technology and the perspective initiation at OSR, and I am certain within the other government research communities, the initiation of a significant research program thrust in this problem area.

I think that's the objectives that OSR has in mind for why we are here today. We anticipate that there will be a formal proceedings coming out from this Workshop. We had a great deal of interest in the meeting, and within the guidelines of what we tried to organize there was only room for so many people.

WORKSHOP ORGANIZATION

Structure/Property Correlations and Models
Constitutive Properties
Failure Processes
Experimental Methods
Nondestructive Testing

W-6

WORKSHOP OUTPUT

Identification of Research Goals

Apparent Research Approaches

Not So Apparent Research Approaches

Research Emphasis:

Needs vrs opportunities match up with
technology

Perspective initiation of research program
thrust

W-7

Having a formal proceedings from this meeting will allow us to present to a larger segment of the community the results of the discussions here during the next few days. I will answer any questions if anybody has any at this time, and if not I will turn the floor back to Dr. Pipes.

DR. PIPES: Thank you very much, Bill. I think our objectives for this Workshop are now clear. Let us go ahead and introduce our first speakers. We have, as you see, speakers to talk about Air Force programs in this area, industrial efforts, and also Navy and Army programs. Let us begin then by introducing a person I think everyone in this room has either met or knows of by reputation, Dr. John Halpin, now of the Air Force Flight Dynamics Laboratory. It gives me a great deal of pleasure to introduce John at this time.

B. USAF AND INDUSTRY PERSPECTIVE

1. Air Force Laboratory Programs

a. Air Force Flight Dynamics Laboratory Perspective

DR. HALPIN: Good morning. It's a pleasure to be here. I'd like to review with you for a few minutes the results of evaluations that we have been performing and the formulation of planning activities as to how it would impact the sessions today. I think on the first viewgraph [Ed. note: The viewgraphs of Dr. Halpin's presentation are not available] the important point that we'd like to make is that we are interested in resin matrix composites primarily because they do something for us. We get an advantage in the aircraft construction and it's that potential

for systems improvement, be it in either aircraft or other art-
that civilization uses, that we invest in the R & D. We are
looking at it in two senses: the high structural efficiency
offers us a potential improvement; the moldability that we have
with polymeric materials in the form of composites provides
us an avenue to achieve a high performance level in a vehicle
with the possibility of reducing costs. And in today's environ-
ment we are going into a resource-limited world, energy and
financial, and the capability of even making a performance
level and controlling the cost is a significant driver to the
people in the Department of Defense. Recognize, however, that
in exploiting new technologies, and really we are looking at
polymeric materials for the first time in primary space-flight
applications, that up until this time the only real area that
polymeric materials have been used in primary structures has
been in automobile tires and in parachutes. So we see, really,
a revolution taking place in our day, very similar to when
structural steel came in at the end of the last century.
However, we do have some issues that are slowing down or con-
trolling the rate at which we can exploit the technology, and
a great number of those issues are technical issues, mitigated
by the normal problems of how you develop efficient production
operations, development times, and potential impact on the
ownership and the operational usage of vehicles.

The next viewgraph illustrates what we see as the

advantages in the technology. Primarily, the high strength and stiffness-to-density ratios that you see out of these materials that were recognized in the early sixties that led to a series of structural development programs which have demonstrated that about a 20 per cent weight reduction is possible when you build a structural part out of a resin matrix system reinforced with graphite or another type of a high-modulus fiber system.

This weight reduction is factored through the airplane. If you reduce the weight of one part you can reduce the size of other parts in the vehicle, you can effectively resize the vehicle, if you like.

So, it's possible to take this weight reduction and convert it to a weight reduction on the entire vehicle itself on an order of 10 to 15 per cent on resized vehicles. That resizing produces the option for the performance improvements, which we will get into a little bit later, or the reduction in the cost of the vehicle itself.

The same thing will happen in the commercial area where the weight of the American automobile will be reduced to control the fuel economy of the automobile. The objective right now is to reduce the weight by about seven to nine hundred pounds on a standard American vehicle, and in effect the automobile industry will go in the same direction as the airplane, to higher efficiency structural materials.

At the same time, we are looking at propulsion systems, but in order to make an airplane fly you have the balance of

the forces, and the weight and the thrust are primarily what we are dealing with when we are in materials technology areas.

The thrust comes out of the engine. We are looking at the engine by using advanced materials in the engine of a 25 per cent improvement in the thrust-to-weight ratio, and to give you an idea of that impact, that's rated in a 10 per cent change in the total gross take-off weight, we redesign the airplane for the change in the performance of the engine itself.

So, by changing the power plant you get approximately the same pay-off as by changing the entire structure of the vehicle itself. The impact that we see on our force systems right now is if we resized a vehicle with these technologies to build a high performance fighter for military air-to-air combat, you can develop an airplane if you convert it to this technology so that the conversion in an air-to-air combat, the effectivity of the fighter would be about two-to-one advantage with the lighter weight, higher performing vehicle.

In a total life cycle cost, we are looking at a potential pay-off of 8 per cent life cycle cost.

A typical aircraft fighter system we may develop will involve a 15 to 20 million dollar investment over a 15-year life cycle, and that means approximately a one-and-a-half billion dollar savings by maintaining a competitive performance level and using advanced technology.

These are the incentives for us to move out of the metallics area into the reinforced polymeric area, and in

some cases into reinforced metallics in engine design. So there are very real engineering savings.

The next view graph is the other side of the coin. With this attractive potential there to exploit, we have to develop the understanding and the methodology to achieve that potential. As a result of a series of discussions the Air Force and in fact the nation, the engineering public in the nation is convinced that the potential is real, that the feasibility for the technology has been demonstrated. But there are a series of problems that have yet to be overcome to achieve full commitment to the technology itself.

At these points here the total Air Force summary and the fact that this was an industrial assessment as well revolves around a series of problems that have developed - well, not really problems - the first set of trial items that were put into service is to get a feedback from the service condition. We solved some minor durability problems, no safety-in-flight problems. Primarily, this was learning how to develop the appropriate resin systems with the necessary environmental durability and the ability to develop screening procedures, what we call qualification testing, which would be sensitive to the characteristics of the polymeric resin system and the fiber systems and identify ahead of time what the life-limiting attributes of the system would be.

And for us in the polymeric area this doesn't seem to be a mysterious process, but as I pointed out you must realize that the people who develop vehicles worldwide are

basically metals oriented people. Their instinctive background is in metals technology. When they work in structures they think metals, even though they are saying and reading composites and polymers and adhesives and that sort of thing. And the natural reflexive reaction is to manage the program as if you were managing a mechanical structures development program.

That goes also for development testing, the qualification testing and the certification of the reproduceable quality of the product itself.

We have seen some minor issues that have developed. They are not minor if they are left unidentified, but they are minor in the perspective that obvious changes in approaches to handling that development program will rectify them.

Just recognizing that when you change materials technologies you change sensitivities and therefore you change the way in which a man should handle and test for problems in systems. And so it's a developing of an understanding, a familiarity and a reaction, and this is what we in the research community do. We identify issues, we develop an understanding and we help to transmit this information into the engineering public to facilitate their ability to use the product.

Laboratory data has played a role, as well as the service data in identifying those types of issues. In other areas we found that while we have a qualitative understanding of physical phenomena in polymeric resins that affect the performance in the non-metallic area, in many cases we do not

have the complete analytical methodology that's required to support the engineering design, particularly in composites in terms of structural safety and durability area. We don't have a large history in primary safety applied applications, we do not have an extensive background in fatigue, cumulative damage processes, and other types of calculations of this type to support a 20-,30-year operating life-designed projection for the vehicles.

In the other areas in terms of systems integration you get into a different set of physical problems other than the basic durability, the strength, fatigue resistance of the materials.

In a non-metallic system you have a different bonding backbone than you do in a metallic system, obviously, and the important point there is not only for the high specific properties but the electro-magnetic character of the material is changed once you move out of the metallic bonding system into a covalent bonding system.

It's another one of these basic reflexive assumptions that metals conduct electricity and they provide shielding from magnetic fields. When we move out of a metallic structure we take away from a structure the natural ferro cage that that structure has. In any automobile, in any ship, in any train, in any airplane, you have internal power systems, internal electrical control systems.

In advanced aircraft we are moving further into this area just like the cash register is doing. You have seen the

change in the cash register from a mechanical device to a totally electronic device.

In the F-16, which is under development today, and in portions of the B-1 we are going from pneumatic and mechanically driven flight controls into completely electronic flight controls, which we call digital fly-by-wire flight control systems. We have the normal navigational and the target acquisition, the radar. What this means is it's one big huge flying computer in the air, flying through a highly electrified atmosphere, being struck by lightning, seeing weapons countermeasures by the enemies, and now you have a total change in the physics of the structure.

We don't know for sure that we have any problems at all, but the fact that the basic physics of the airframe itself, which provides a natural shielding, does raise concern in our systems development people. They have concerns even in the metallic structure going into an all-electrified controls systems.

So we have unknown systems integration effects. What we are now looking at is the physics of the electro-magnetic characteristics of the structure and how it interacts over the entire vehicle, and the simple thing is if we have computerized circuits at different positions in the airplane. How do you get an equal potential ground plane so that the equipment doesn't talk back and forth to each other?

The rest of these are basically the industrial problems. This one is where the payoff is to us in terms of the tech-

nology, and I don't want to de-emphasize this, a probable need to expand the development, engineering, and testing, which is the qualification and certification testing, the development cost, and the schedule.

Now, the things that develop in here are unknowns, uncertainties, loose ends that want to be developed and haven't been developed yet. I don't mean that you can't use the technology. It's been proven empirically why by trial and error that you can successfully build satisfactory structures which will meet the safety of flight requirements.

But by having a lack of understanding, a lack of development experience, a lack of scientific experience that hasn't matured yet - a lack is not a proper word. We are in a normal state of development. We are like teenagers. We have established many characteristics of our adulthood but we haven't matured as adults in this technology. So we are going through our teenage years. That creates a certain amount of inefficiency and that inefficiency shows up in the management level right here. It takes a lot longer to do the job and it takes more money to do the job.

Now, when you are in a resource-limited environment, that is a very serious inhibitor to us in the research community, getting the engineering community and the political community to support and incorporate our technology into the next engineering development stages. Because the people who are in charge of developing these systems have serious problems, they are shrinking in dollars and they are shrinking in development time.

In fact, when we introduced a new technology we had a learning process that takes place. After you develop and use things for a while you become more proficient. In competing against metallics, even though you can show that in the final end you may have a better product, it costs you more to get to that better product, and there is a low incentive for the decision maker to go that route.

If you are not quite sure how to get there, with the possibility it is going to cost you more, you know it's going to take a little longer, and you are not quite sure what kinds of problems you are going to run into, then you introduce an element of risk. So you had a cost factor plus an uncertain element of risk, and that is the kind of problem that is a barrier to putting in a new research technology into vehicles themselves. And this isn't an airplane problem, it isn't a Navy problem, it's everybody's problem in the research community. We are seeing it here because we are trying to force, in effect, a revolutionary change in the structures themselves.

Well, we have listed these as concerns because we don't see any of them being show-stoppers, there is no fundamental reason on any of this list why the technology won't be incorporated. It controls the rate at which we will use it, and therefore we list them as inhibitors in that sense over here.

Next chart here goes a little more into detail over some of the issues that Bill Walker just pointed out. In

defining these issues there has been a series of exchanges in the government, the university, the government organizations, the universities, and the last major Air Force discussion with you people was at the Battelle Workshop.

Some of the typical issues that are appropriate from here is the moisture, temperature, processing, sensitivity of resins themselves. Engineers are used to working with metallics and at sometimes the polymer people even forget that they are working with a polymer and a very simple thing like glass transition temperature of a resin sometimes gets overlooked. The fact that the glass transition of the resin is very sensitive to the additives and the kinetics of the curing process, as Dr. Augl pointed out at Battelle, which we all know but tend to forget, the fact that if you put a plasticizer in a resin it depresses the glass transition temperature of the resin, just like alcohol depresses the freezing point of water. These things impact the static design capacity and the fatigue resistance of the structure. They are typical of the kind of problems that develop, the loose ends that we tend to overlook, but which are fundamental in developing healthy structures.

Another interesting thing is the fatigue resistance of materials as dictated in the tension case. You will see this later by the characteristics of the fibers themselves. The fibers tend to be ceramic and graphitized carbon materials. So we have positive fatigue advantage there.

But what has happened in laminated solids is a tendency on the compression side to generate out-of-plane tensions

normal to the lamination planes, and this produces a potential fatigue sensitivity in the compression areas. So, in a metallic aircraft wing, for example, we have a great deal of fatigue cracking on the tension side. Composites cures that problem, but it produces an equivalent sensitivity on the compression side. We don't know the magnitude of that.

Another interesting problem which we have to face, and metallics people have to face as well, is that if you do develop a potential failure process which could limit the life of a part or limit the static strain capacity of the structure due to errors in the production of the part, you must have some device to inspect it. Now, in some areas because we don't know how to detect the manufacturing errors, right now with inspection techniques we are looking at proof test technology. In any event, the design of the proof test or the censoring of an article through a non-destructive inspection procedure requires an understanding of the physical character, the variations from the norm, and how they affect the failure process of the material. This includes not only scratches and delaminations, but simple things like mis-stoichiometry, unequal temperature distribution through parts during the cures, exotherms, and this sort of thing. The typical one that we are all familiar with, or really not familiar with, is just simply an adhesive joint. I take a film of adhesive and I study it. I can prove to you that a film of adhesive fails by a cracking process. It fails from pre-existing flaws and it fails through all the formal fracture mechanics fatigue

methodology, and if I inspect that film I can find it and I can reproduce for you the entire metallic technology right on that film. I then take that and I slap it in between two substrates, bonding two different materials together, and I haven't changed anything about the failure characteristics. I have changed maybe the state of stress. But I have lost one important thing. I can no longer see that pre-existing flaw, and I can no longer follow it growing, and I have converted an inspectable, measurable failure process into a noninspectable process.

Now, on an engineering design, and in the use of structures it's not required that you have a structure which has zero probability of failure. It's only required that you have an understanding of what limits it and how to look for it, and having recognized some process developing having a decision-making apparatus which tells you when you can or can't use the structure.

The problem that you get into is that we will be going into some structures utilizing integrally molded complex shapes of the type we'd like to use to reduce the price, by using the natural characteristics of polymeric systems, but we tend to take away that very valuable ingredient, inspectability. But, in balance, inspectability is somewhat of a myth in metallic structures too. Inspectability is there if you know where to look and how to look. If something happened that you are not aware of we often miss it there too, so I don't want to overdo it.

Uncertainty in the analysis methods, again, we mentioned that.

Next view graph has come up again and again, and I tried to make the additional comments here that keep going in perspective here. There are identified technical issues which need to be resolved, that in balance here we see a verification of the very high strength-to-weight and modulus-of-weight ratios. We have seen that the tension fatigue problem just doesn't exist in these systems either environmentally induced or stress-induced, that the development of cracks and extension of cracks from notches on fatigue surfaces doesn't take place as it does in a bulk polymer or in a metallic. That the environmental effects that you will see today are real, they are really the manifestations of the normal effects that you would see by putting a diluant in a polymeric solid. They must be accounted for, and the major impact today has not been that you can't use the technology, it's been that the temperature limits and the design stress levels that you can use, design and structure end, has been reduced, and that reduction will ultimately impact the types of vehicles that you can apply the technology to, unless we have a growth in materials technology as well as in descriptive and analysis techniques.

Engineering, data collection, engineering analysis, tells us how, which ways we can use the materials technologies that we have at hand today. In order to change and expand the design realm for the material we have to have a change in

materials technologies as well, and what these experiences are telling us is that we need to have a parallel effort in the development of better resin systems to expand the design envelope, because we have found a constraint in that envelope.

The current position today is we have expanding applications, they are very conservative designs, in the future they will be looked upon as engineeringly inefficient, but they provide a margin of safety to protect us during the early application stages of the technology.

What we want to achieve and need to achieve to provide a continuing aggressive movement in the area is improved understanding of the physical phenomena that give rise to these concerns, and that is why we are supporting the basic research effort. We are looking here at AFOSR, and the basic research, to provide the basis for the scientific understanding. We are really keying more and more into emphasizing understanding and de-emphasizing trial and error and empiricism.

The point I have tried to make in the definite development of those inhibitors is that you can do it without understanding, but the process of doing it is very inefficient and very costly and eventually will keep us from exploiting the technology for that reason. So you play a key role in the basic research and exploratory development areas in developing the understanding which makes the process of converting technology into engineering and efficient process, and therefore, we keep our research apparatus alive by that mechanism.

Now, we, from the engineering side, want to see a

better understanding here of the materials problems as well as the analysis problems, how to develop affordable higher temperature matrix systems and moisture resistant systems, given the fact that you have got a plasticization once water gets in there, you are going to use Tg's, and to control the rate at which you get water in, you can control the levels of water absorption, you get higher temperature materials which will process like epoxies so that you can use comparable technology.

I have pointed out we will be looking to develop from the engineering side improved analysis techniques to provide for life prediction and inspection procedures. The Air Force is conducting an extensive five-year program to support a whole variety of issues and it's formulated in this format here. We identify these inhibitors. They directed specific programs at the engineering development, at the structural development and systems application levels to try to attack these inhibitors here.

We have emphasized very heavily technology improvement. We have got about 150 million dollars going into composite technology between now and the end of 1980. In doing that we have expanded the budget and in the expansion we have added about 25 million dollars in that time period to emphasize scientific and technological advancement in the area.

Supporting that in this area here, we are pushing more aggressively to get hardware into structure on the B-1, on the F-16, and in some space applications in some other areas. That's primarily to look at production costs, operation

and maintenance experience, in which you have to develop full-scale hardware, you have to get it into service, you have to get a feedback from the service operation.

We have existing hardware which we are looking to extract more of the information about the environment, about the durability issues, and in turn to use that as a test of what our scientific understanding that we develop here, whether that translates into service experience that's obtained here and here.

In keying in demonstrating to our engineering people that we in the polymeric community, in the structures community, recognize the difference between a non-metallic structure and a metallic structure, we recognize the different ways in which they need to be managed, and the management here, I want to emphasize the other thing, which is unique to the Air Force in a sense, we are a research organization. We are a development organization in that we develop airplanes. But we don't sell them to people. We buy them back and we use them. So we are a user. So we are like Bell Laboratories in the civilian world.

We have to satisfy all of these different areas of activity equally to accept the technology. The major problem we come into not only is producing inefficiently but providing the user, which are the operating commands and the maintainer of the logistics command, with the keys in which he can use to identify potential polymeric, what is the right way to manage a polymeric structure, how to maintain it for

30 years with the same level of activity that he would invest in metallic structures.

In order to win a commitment we have to show him a scientific understanding in advance of the commitment, because once he has signed on the dotted line to buy the system he has bought a series of problems whether he wants them or not. So, in effect, we have to prove that we can control the problems, and that is the driving force behind here, supporting this. This series of activities is the other technical activities in other government agencies.

Now, for the industrial people, I want to point out that we have very extensive critical hardware development programs which have been typical of what we ran in the past. To convert to technology you have to go through the structural development process. That identifies technical activities as well as developing the background. The important point is in the looking forward and turning against technical issues we are going to maintain this same level of component development that we have in the past. We are not going to diminish that effort.

What we have done is we have expanded this effort, that is really why you are here today, because we are asking AFOSR to expand this effort to complement that activity.

Technology demonstration means that pure technology is so powerful that instead of evolving through, putting a door on here, an empannage on them, a wing on someplace else, that your payoff is so powerful that instead of evolving

commitment, evolution through experience, that you might want revolution, which is go out tomorrow and build an all non-metallic airframe, an all composite engine.

In order to do that, to convince the engineering public, we would have to develop a demonstration vehicle, just like Detroit. They have all plastic automobile cars going around as demonstrators and that is what these programs are here.

The general thrust of the Air Force program, however, is evolutionary, evolving through this area, and through this area here. We are looking at affordable performance levels. The keymark here is not only that you can put out something that is lighter, stronger, and swifter, but it's got to cost the same. It's got to be able to be developed in the same length of time. It's got to be able to be used with the same support moneys. And that is really the crunch and that is why we are emphasizing the thing.

In the past we could just put out the same that was bigger, stronger, and swifter. We could sell it, because absolute performance drove new technologies. But today economics, resource limitations, control that technology transition and the rate of that technology transition which in turn controls the level of the R & D budgets and the basic research community itself.

I think I will just go to the last slide because we are running short of time. I think instead of going through some of the programs the things that we at Wright Field, we are the research and development community for aircraft, we

look to AFOSR for the scientific understanding to define the technical issues here that control the key decision-making processes in the material development and the structural development operations, the keys for monitoring the structure once it's in service, we want that to be based on understanding and not on empiricism for basically the simple reason we cannot afford the inefficiency of empiricism. In the early stages we will do it, because we have no choice, by empirical methods.

But basically what we want here is to identify the issues, develop that understanding, and define from that understanding suitable technical approaches to attack the issues that have been identified and attempt to resolve those issues, because it's only through an improved efficiency in this area, coming out of the basic research areas, that we are going to see continued technology growth in this country.

And this coupling between the basic research area and providing an understanding in which the scientifically oriented engineer can use will be the mechanism to keep a healthy R & D budget in this country and keep the progress. And this is why we at the Field in the engineering development work very closely with the AFOSR, encourage them strongly in this area, and we are looking forward to your deliberations and we look forward to working with you as a team in the scientific community as a whole. And this is what we would like to see.

We wish you good luck. Thank you.

DR. PIPES: There are of course two agencies of the Air Force that are actively or possibly more actively pursuing composite research. Our second speaker to talk about Air Force programs is Dr. Ted Reinhart of the Air Force Materials Laboratory and the Non-Metallic Materials Division.

Ted.

b. Air Force Materials Laboratory Perspective

DR. REINHART: Thank you very much, Byron.

One of the things that Byron didn't tell me was that I had to follow John Halpin on the program and we know, everyone knows, John Halpin; but I think at the Materials Lab we know him a little bit better than most of you, and we know that in 45 minutes John's really not even wound up yet.

Thanks for saving a few minutes, John.

I tried to go through my 45-minute pitch and cut it down so that I wouldn't cover any of the material that John had and so that we wouldn't intrude too much into the coffee break. There are three or four things I'd like to say to you this morning.

Firstly, I'd like to kind of scope or acquaint you with the moisture resistance problem. Second, I'd kind of like to review the conclusions of the Battelle meeting. If you weren't there it might be of interest and if you were there maybe you didn't realize that we came to any conclusions at all. I'd kind of like to review some of the data that we have gathered since that meeting, and I hope other people will do the same during our sessions here. And then lastly I'd like to review some of the programs the materials lab has going, to try to understand and to defeat this moisture problem.

Turn on the first one, please. (R-1)

Firstly, I'd like to scope the moisture resistance problem for you.

Next one, please. (R-2)

MOISTURE RESISTANCE CHARACTERISTICS

LAMINATING RESINS

R-1

PROBLEM

RESIN MATRIX MATERIALS

—ABSORB MOISTURE UNDER AMBIENT EXPOSURE CONDITIONS

—ABSORBED MOISTURE CAUSES DEGRADATION OF RESIN
PROPERTIES AT ELEVATED TEMPERATURES

- REDUCES T_g
- REDUCES MODULUS VIA PLASTICIZING EFFECT

—ABSORBED MOISTURE CAUSES DIMENSIONAL CHANGES

R-2

We know that our existing epoxy matrix materials and, in fact, all of our organic matrix materials absorb moisture under various conditions of exposure to humidity. This absorbed moisture does several things. It causes a degradation of the resin properties. Sometimes at room temperature we see this, more specifically at elevated temperatures it takes place. It reduces the T_g , and I will try to explain for those of you a little later that might not be too familiar with what a T_g is. It reduces the modulus, as John mentioned, via the plasticization effect. Another thing we don't really have a good handle on. The moisture absorbed causes dimensional changes. We don't know what influence this has yet on the design.

As a result of moisture pickup now, (R-3) we have mentioned, we suffer losses in matrix mechanical properties and specifically in the composite we lose composite properties where the matrix dominates.

We see a severe reduction in interface controlled properties and this is the 90 degree tensile properties and in interlaminar shear degradation.

I mentioned we sustain a dimensional change. Our adhesional bond has demonstrated increased rates of stress relaxation. Here again fiber-dominated loading modes, as we will see a little later, don't change significantly. The failure modes change, but the properties don't, and we will talk about that a little later, too.

We have already defined that our composites, and our

PROBLEM

RESIN COMPOSITES

- AS A RESULT OF MOISTURE PICKUP BY RESIN, COMPOSITES:
 - SUFFER LOSSES IN MATRIX CONTROLLED MECHANICAL PROPERTIES
 - REDUCTIONS IN INTERFACE CONTROLLED PROPERTIES
 - SUSTAIN DIMENSIONAL CHANGES
 - DEMONSTRATE INCREASED RATES OF STRESS RELAXATION
* AND CREEP
- FIBER DOMINATED MECHANICAL PROPERTIES NOT AFFECTED,
BUT FAILURE MODES MAY CHANGE

resins have a moisture problem. (R-4) The characteristics in the resin that we think are responsible for the moisture pick-up are these active groups. All of our epoxies and all of our polyimides have various amounts of hydrophilic groups. We also understand some people feel that even the aromatic groups can attract and bond the moisture. I have had conflicting opinions from various experts here. Maybe this could be discussed a little bit later. Does the aromatic ring itself really absorb moisture? Does it attract moisture? There is some question here.

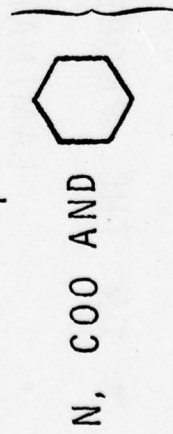
I'd like to, for a few minutes, compare the effects of moisture, and the amount of moisture picked up by the various resins that are available to us today for use in composites. (R-5) Primarily, all we are using today are the epoxies. There is quite a bit of work going on in the Navy and in the Air Force on the thermoplastic resins. Modified epoxies, polyimids, and hydrocarbons are available and not being used right now primarily because there is a lack of data on them.

Let's orient ourselves here. If we look at moisture absorption of epoxy resins on the neat resin casting as a function of time. (R-6) You will see that the three popular resins being used in composites today pretty much fall into the same area, and there is a good reason for this, because all these resins are nearly chemically the same. The 3501 has an accelerator, which the 5208 does not have, but that's only a minor portion of the formulation.

ALL RESINS THAT PROVIDE HIGH PERFORMANCE
COMPOSITES ABSORB A CERTAIN AMOUNT OF
MOISTURE

POLYMER CHARACTERISTICS RESPONSIBLE FOR GOOD
COMPOSITE PERFORMANCE ALSO RESPONSIBLE FOR
MOISTURE PICKUP

$\left. \begin{array}{l} -\text{OH} \\ -\text{O}- \\ -\text{N}- \\ | \end{array} \right\} \text{GROUPS ATTRACT AND STRONGLY HOLD HOH}$



GROUPS ATTRACT AND STRONGLY HOLD HOH
BY π BONDING

R-4

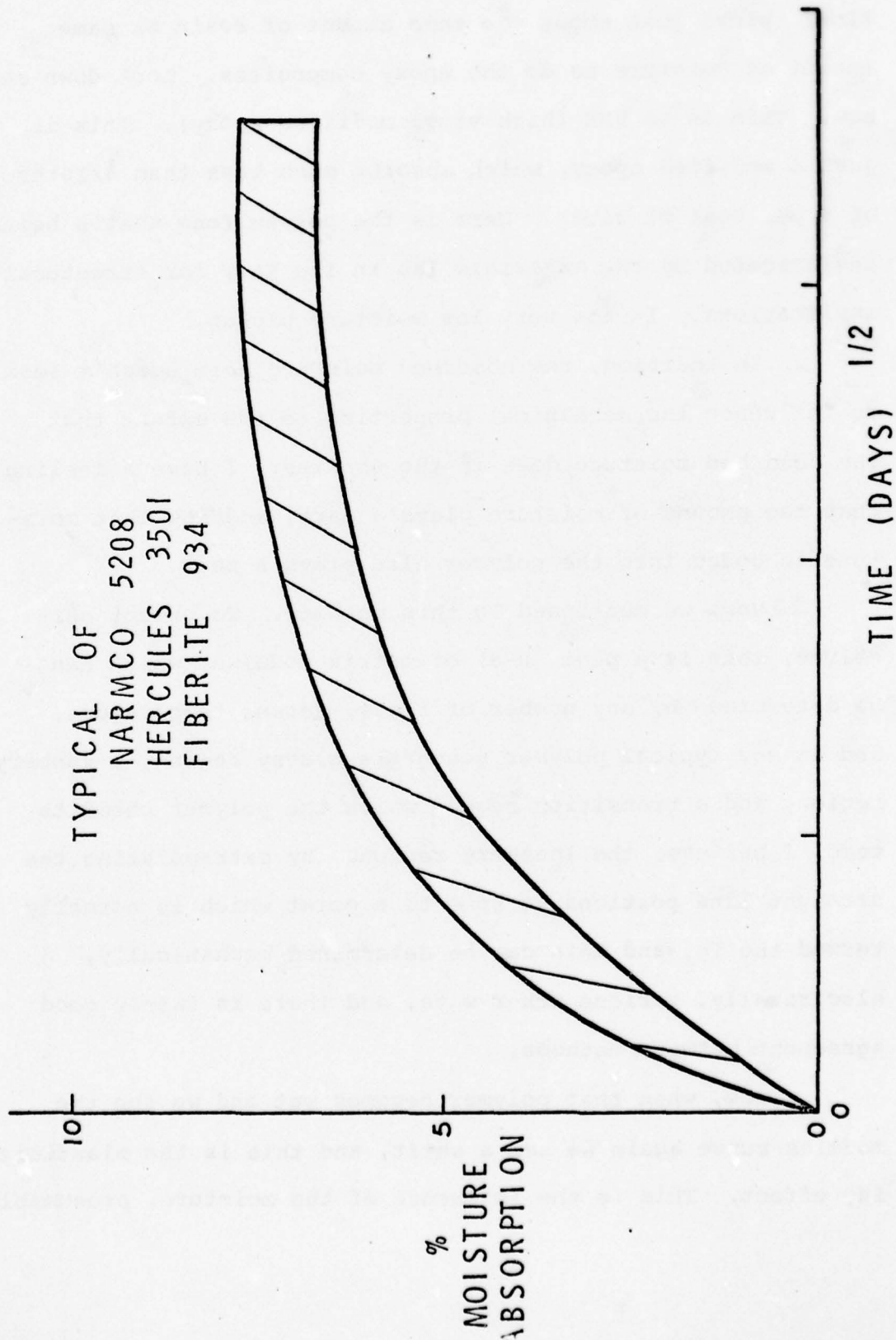
COMPARISON OF EFFECTS OF MOISTURE
ON THE PROPERTIES OF VARIOUS
LAMINATING RESINS

- EPOXY RESINS
- THERMOPLASTIC RESINS
- MODIFIED EPOXY RESINS
- POLYIMIDES RESINS
- HYDROCARBON RESINS

R-5

MOISTURE ABSORPTION OF EPOXY RESINS EXPOSED
120°F - 95% R.H.

TYPICAL OF
NARMCO 5208
HERCULES 3501
FIBERITE 934



R-6

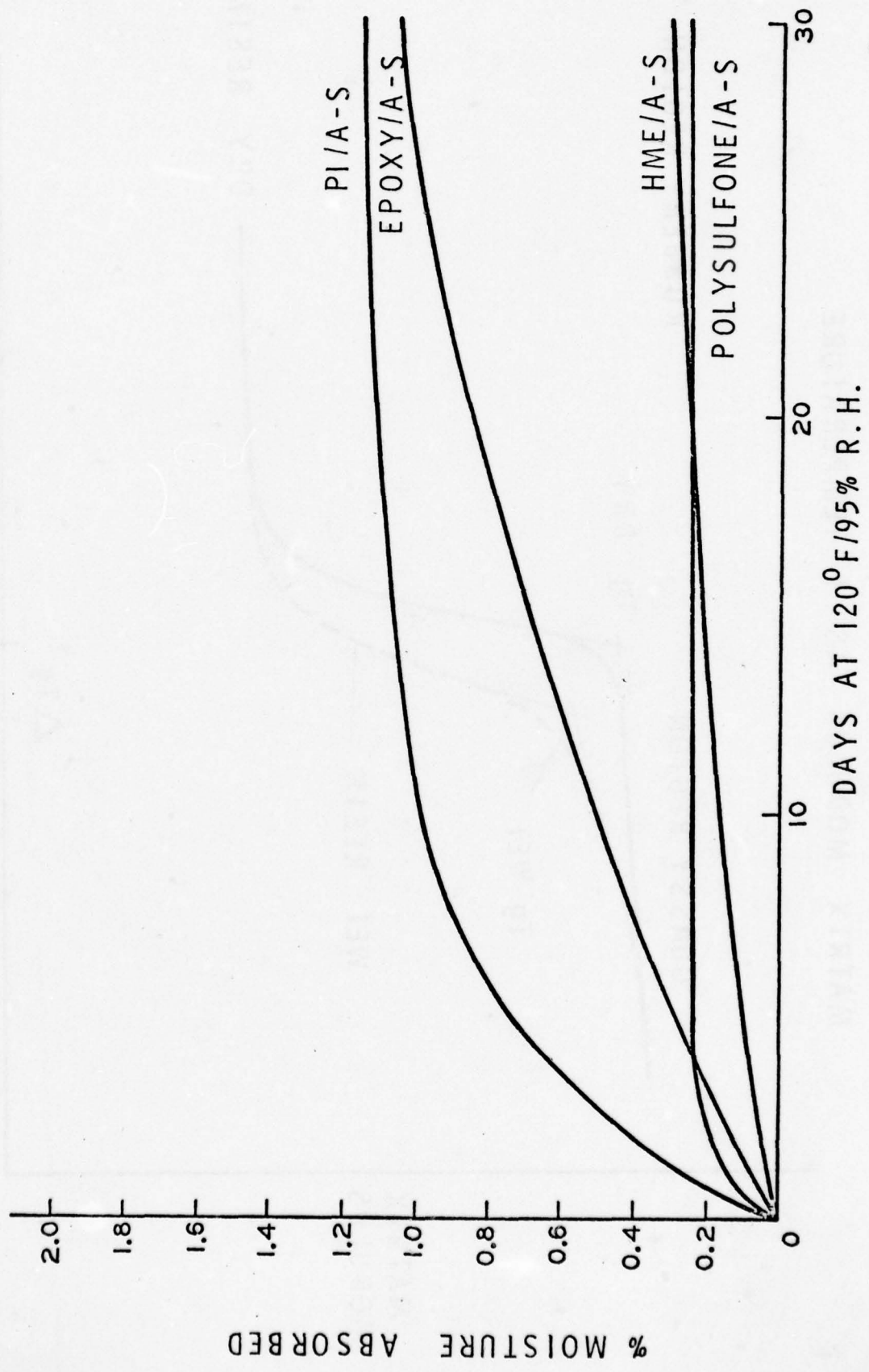
Now, let's look at the moisture pickup of composites. (R-7) Here we can see a polyimide with the AS type graphite fiber, picks just about the same amount of resin or same amount of moisture as do the epoxy composites. Look down here now. This is an HME (high vinyl modified epoxy). This is just a modified epoxy, which absorbs much less than 4/10ths of a per cent of water. Here is the polysulfone that's being investigated by the materials lab in the Navy for structural applications. It has very low moisture pickup.

In addition, the absorbed moisture here doesn't seem to influence the mechanical properties to the extent that the absorbed moisture does in the epoxies. I have a feeling that the amount of moisture plays a part, and how that moisture is bound into the polymer also plays a part.

Now, we mentioned Tg this morning. To orient ourselves, this is a plot (R-8) of matrix modulus, which can be determined by any number of tests, versus temperature, and in any typical polymer you get a glassy region, a rubbery region, and a transition region which the polymer chemists term, I believe, the leathery region. By extrapolating the straight line portions we come to a point which is normally termed the Tg, and this can be determined mechanically, electrically, various other ways, and there is fairly good agreement between methods.

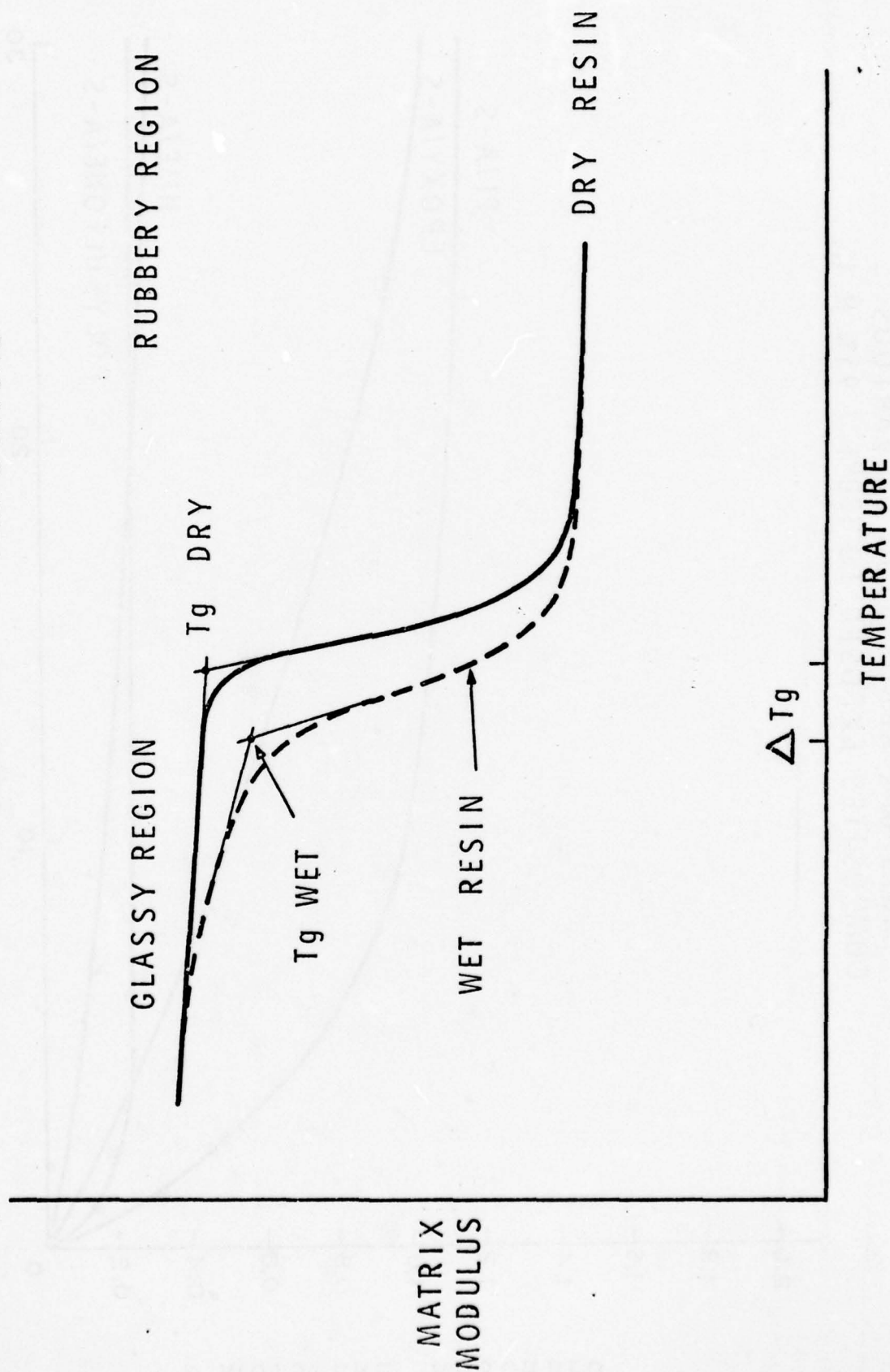
Now, when that polymer becomes wet and we run the modulus curve again we see a shift, and this is the plasticizing effect. This is the influence of the moisture, presumably,

MOISTURE ABSORPTION OF VARIOUS
COMPOSITES EXPOSED TO 120°F / 95% R.H.



R-7

MATRIX MODULUS AS f TEMPERATURE



disorienting the chains, breaking up hydrogen bonding to the chains, making them less attractive to one another. And this is the ΔT_g that we see due to moisture pickup.

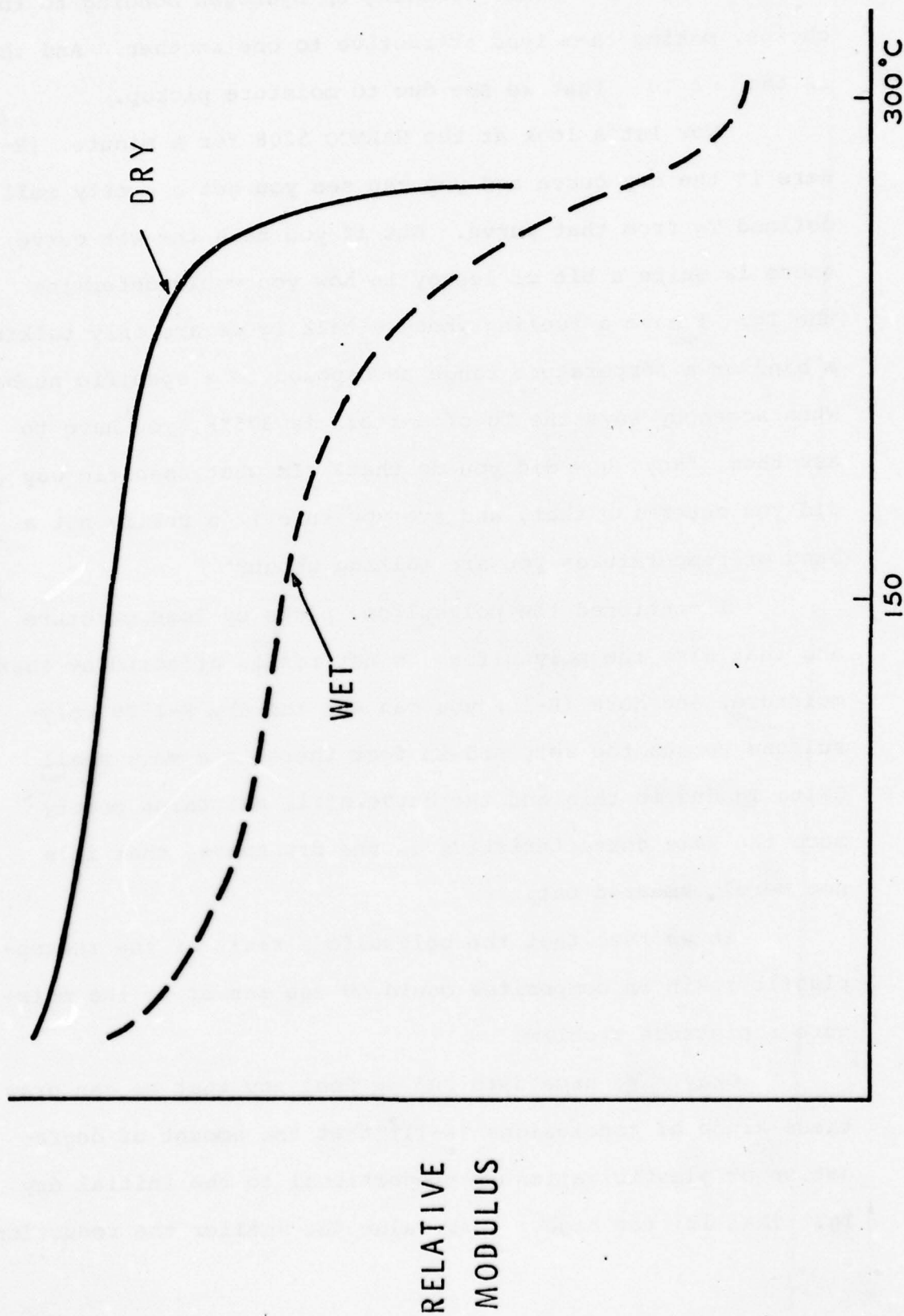
Now let's look at the NARMCO 5208 for a minute. (R-9) Here is the dry curve and you can see you get a pretty well defined T_g from that curve. But if you take the wet curve there is quite a bit of leeway in how you would determine the T_g . I have a feeling when we talk T_g we are only talking a band or a temperature range as opposed to a specific number. When somebody says the T_g of a resin is 375°F, you have to ask them, "Hey, how did you do that? In what specific way did you determine that, and are you sure it's really not a band of temperatures you are talking about?"

I mentioned the polysulfone picks up less moisture and that also the polysulfone is not really affected by that moisture, and here (R-10) you can see the dry P-1700 polysulfone versus the wet, and in fact there is a very small Delta T_g due to this and the curve still maintains pretty much the same characteristics as the dry curve, that it's not merely smeared out.

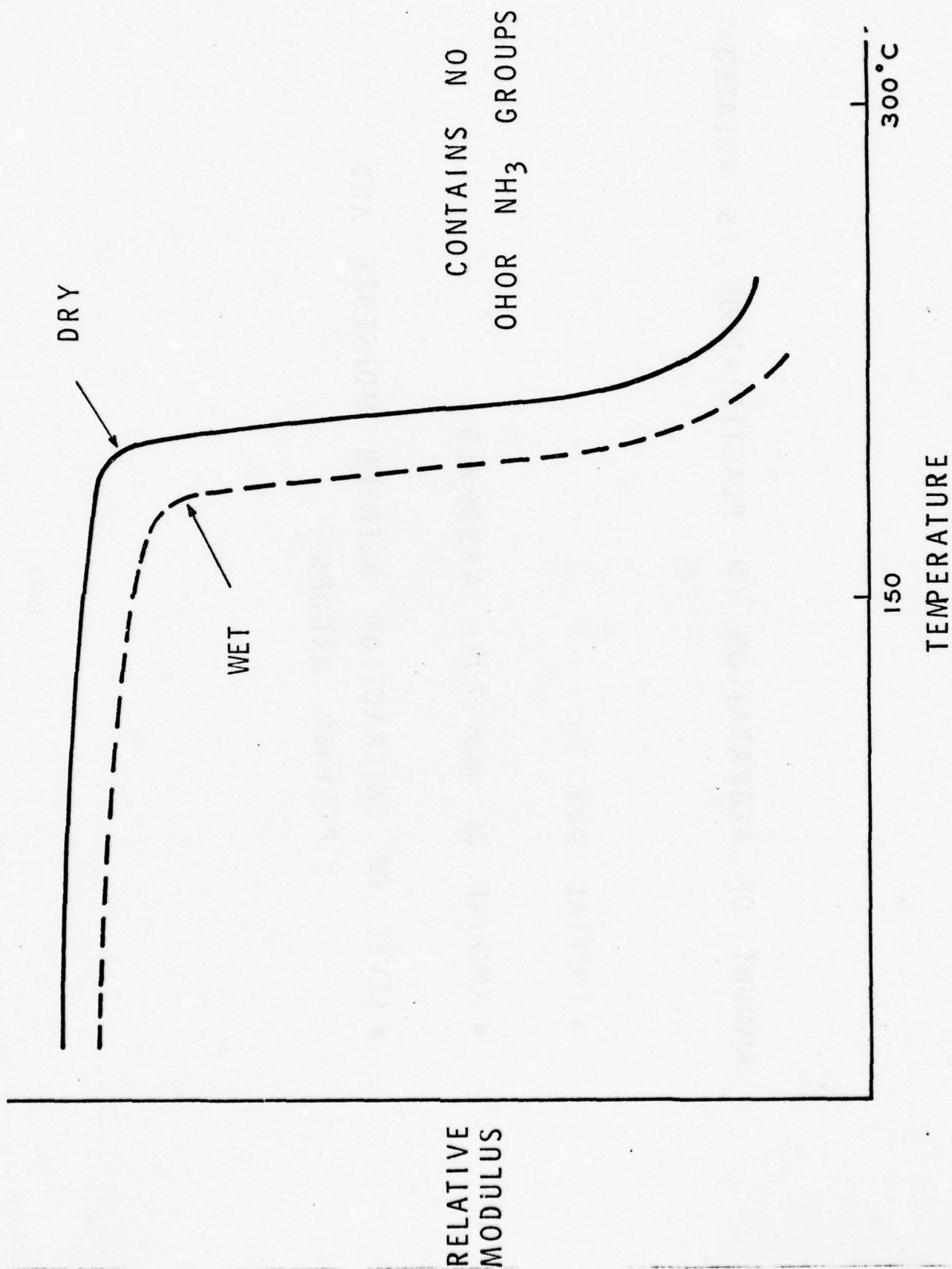
So we feel that the polysulfone resin or the thermoplastic resin in composites could be one answer to the moisture resistance problem.

Okay. We have data and we feel now that we can draw these kinds of conclusions (R-11) that the amount of degradation or plasticization is proportional to the initial dry T_g . That is, the higher this value the smaller the reduction

NARMCO 5208



PI700 POLYSULFONE



AMOUNT OF DEGRADATION OR PLASTICATION IS RELATED

TO:

- INITIAL DRY T_g
- AMOUNT OF MOISTURE ABSORBED
- LEVEL OF INTERACTION BETWEEN MOISTURE AND
POLYMER GROUPS

R-11

in Tg that we see. And here processing plays a very important part in the dry Tg of the material. Some manufacturers recommend that you post-cure the resin and 5208 gets a post-cure of two or three hours at 375 or 400.

With the 3501 resin, there is no post-cure recommended so its cure might be four hours at 350, and I will show you some data a little bit later to point out that this post-cure has a drastic effect on mechanical properties after moisture exposure.

The degradation, of course, is a function of the amount of moisture. One of the things we are trying to look at now in the lab is where does this moisture go, how is it attracted, how tightly is it bound to the chains? Hopefully, once we understand the mechanism of moisture attack we will have some way or develop some way of defeating this.

And as I mentioned before, the effect on the polymer is related to the level of interaction. If it's tightly bound, we are sure that the effect is going to be drastic. If it's loosely bound, like in the hydrocarbon resins or the polysulfone, the effect is going to be minimal.

Okay. What are some of the routes presently available to us (R-12) to negate or avoid this moisture problem? One, the one that John talked about this morning, we are generating data, hot wet design data. This amounts to the use of a knock-down factor or a safety factor in the design of a composite structure.

We can use the high Tg polymers. We have the addition

SOLUTION

ROUTES PRESENTLY AVAILABLE BY WHICH WE MAY CIRCUMVENT,
AVOID OR ELIMINATE THE EPOXY MOISTURE PROBLEM:

- USE OF DESIGN KNOCKDOWN FACTORS ADEQUATE TO PRECLUDE STRUCTURAL RELIABILITY PROBLEMS
- USE OF HIGH T_g RESINS (POLYIMIDES, ETC.) WHICH ARE NOT AFFECTED BY MOISTURE AT LOWER TEMPERATURES
- DEVELOP MATRIX RESINS THAT ARE NOT SUBJECT TO MOISTURE DEGRADATION
- USE EXISTING POLYMERS LESS AFFECTED BY MOISTURE THAN THOSE PRESENTLY IN USE
- USE OF PROCESSING CONDITIONS, i.e., CURE AND POST-CURE WHICH DELAY ONSET AND REDUCE SEVERITY OF PROBLEM
- LIMIT USE OF RESINS TO 270°F WHERE MOISTURE AFFECTS ARE MINIMAL.

and the condensation type of polyimides, some of which process almost as easily as the epoxies do. They don't have the toughness that we like to see in epoxies but they are not affected by moisture in the temperature range of our interest, which may be 250 to 350 Fahrenheit.

Three, we can develop matrix resins like the epoxies that have all the good things that the epoxies have but are not affected by moisture. We are working on that, but it's not an easy problem. If it were very easy, the people like the duPonts and Union Carbides would have those products out on the market right now.

We can use existing polymers that are less affected by moisture. We can go to the modified epoxies, to the hydrocarbon materials, or we can go to the polyimides which in the case of engine applications, I believe, that's what we are going to do.

We can use processing conditions, that is the cure and post-cure, which minimize the moisture degradation of our materials, and this means probably protracted post-cures at temperatures of 375 and 400 degrees Fahrenheit.

Okay. Let's move into the Battelle meeting (R-13) and I will summarize in just a few minutes the conclusions that were made.

Go ahead, please. (R-14)

This meeting or workshop was about six months ago and the purpose, as you can read, was to collect and discuss (R-15) the information on the moisture degradation of composites

DURABILITY WORKSHOP

RESIN MATRIX COMPOSITES

BATTELLE'S COLUMBUS LABORATORIES

SEPT 30 - OCT 1 & 2, 1975

JOINT INDUSTRY / AIR FORCE (SERVICES)

R-13

DURABILITY WORKSHOP

PURPOSE:

TO COLLECT AND DISCUSS JOINT VIEWS
AND OPINIONS OF THOSE IN THE COMPOSITES
COMMUNITY HAVING KNOWLEDGE OF THE EFFECTS
OF MOISTURE AND THERMAL CONDITIONING ON
RESIN MATRIX COMPOSITES.

R-14

DURABILITY WORKSHOP

GROUND RULES:

AIR FORCE PERSONNEL TO ACT AS
TECHNICAL CONSULTANTS/RECORDERS/
ASSISTANTS TO PANEL CHAIRMAN AND
NOT ATTEMPT TO INFLUENCE PROCEEDINGS
SO THAT CONCLUSIONS AND RECOMMENDATIONS
ARE THOSE FROM THE INDUSTRIAL COMMUNITY.

R-15

that the industry had at that time. The goals (R-16) here, and they were very ambitious, were to define effects and causes and approaches, and to suggest and organize new materials and programs to bring this problem into better visibility. Our approach here, we divided everyone up into two groups, the materials and processing panel was headed up by Howard Siegel of McDonald-Douglas, and we discussed these kinds of things. The degradation mechanisms, how do we solve it? What kind of tests do we run and how important is raw materials, Q.C.?

The second panel (R-17) was structures and was headed up by Red Maske of General Dynamics, Fort Worth, and these were the kinds of things that were discussed in that panel. Now, personally, I was associated with the materials panel, and I'm not really conversant with all the details that were discussed in the structures panel, but we can review their conclusions anyway.

In the materials panel we came to these conclusions (R-18) and some of them were kind of by the seat of the pants at that time. The first one, we saw no irreversible chemical or mechanical degradation taking place in our composites. Pretty much, the data showed at that time that if we were to dry the composite out, that may mean we have to cycle our airplanes through Yuma, Arizona, every three years, we get all of our dry composite data back, the mechanical properties rise to the original levels.

We came to the conclusion that all resin systems were

DURABILITY WORKSHOP

GOALS:

TO DEFINE EFFECTS, CAUSES, DESIGN
APPROACHES AND TO SUGGEST AND ORGANIZE
NEW MATERIALS AND STRUCTURE DEVELOPMENT
PROGRAMS WHICH COULD LEAD TO RESOLUTION
OF THE MOISTURE PROBLEM.

APPROACH:

TWO SEPARATE PANELS FORMED.

1. MATERIALS/PROCESSING PANEL - H. SIEGEL, MAC
DEGRADATION MECH. CHEM/MECH.
POTENTIAL FOR SOLUTION
TEST/CONDITIONING METHODS
RAW MATERIALS Q.C.

DURABILITY WORKSHOP

II. STRUCTURAL DEVELOPMENT/QUALIFICATION PANEL
E. MASKE GD/FW

GROUND/FLIGHT ENVIRONMENT

EFFECT OF TIME/ENVIRONMENT

LABORATORY SIMULATION

ANALYSIS METHODS

CERTIFICATION

R-17

DURABILITY WORKSHOP

I. MATERIALS AND PROCESSING PANEL

CONCLUSIONS: NO IRREVERSIBLE DEGRADATION MECHANISMS OPERATING.
ALL RESIN SYSTEMS SUBJECT TO EFFECT (DIFFERENCE IN DEGREE).

LIMITED RATIONALE BEHIND EXISTING TEST TECHNIQUES.
EXISTING MATERIALS PROPERTIES DATA - NOT ADEQUATE

DATA GENERATION EFFORTS NEEDED

ACCELERATED AGING

QUASI REAL-TIME AGING

REAL-TIME AGING

RECOMMENDATIONS: IDENTIFY LONG-TERM/REAL-LIFE CUMULATIVE PROBLEMS.

DEFINE ROLE OF INTERFACE DEGRADATION.

DEFINE MOISTURE DISTRIBUTION (PREDICTIVE).

DEVELOP MATRIX RESIN NOT AFFECTED BY MOISTURE.

DEFINE OPTIMUM PROCESS/CURE CONDITIONS DATA

DEVELOP MEANINGFUL/STANDARD TEST/CONDITIONING PROCEDURES.

DEFINE AFFECT OF DIMENSIONAL CHANGES

subject to some degree of moisture degradation. There is a limited rationale between existing test techniques. I think what this means is that at that time everyone was pretty much doing their own thing. Some people would water boil, some people would close their specimens in a pressure cooker at 20 p.s.i. Others would use humidity cabinets at 120° Fahrenheit, 95 per cent of humidity.

I think one of the things we looked for is for this group maybe to point the way to coming up with a standard approach to incorporating moisture into composites so that we can compare data from one company to another, or from one group to another, in the same company, for that matter.

Existing properties data at that time, there was a paucity of data, there still is. We don't have a good handle on the overall long-term properties degradation of composites due to exposure to stress, humidity, and cycles of temperature. And these were the data generation efforts needed. We did need accelerated aging. No one could come up with an idea of what is the standard accelerated test we could use. We need the real time, whether it's quasi-real time or real real time. Our recommendation, define the role of interface, we are working on that one. Define moisture distribution, that's another thing we will talk about in a few minutes.

Accelerated testing gives you a completely different moisture distribution in the composite than does a real time test, and to develop resins not affected by moisture, that's easier said than done. Optimum process and cure conditions,

this is something where there could be a real payoff. And I think this is probably the most important recommendation. Let's develop some meaningful standard test conditions, by that I mean exposure conditions, so we can compare data.

And another one was kind of a charter to the design group as to define the effect of dimensional changes. We have the feeling that the resins absorb moisture and the dimension changes linearly with the amount of absorbed moisture. This is what our data shows us right now.

And, briefly, the conclusions (R-19) of the structural development panel, adequate design information does not exist. That's probably an understatement. Time-temperature environment data is needed. Fatigue, defects, failure modes, all of this requires great definition.

More extensive testing of elements and structures. The materials guys are interested in testing small specimens. The designer, of course, has to go to structural elements and even structural components to get his data, and this is where the real costs are, because you don't build sine wave bars, or you don't build horizontal stabilators and expose them and test them for a few bucks. This is a very expensive program.

An analysis methodology incorporating moisture. One of the things that has to be done is we have to incorporate the moisture in the micromechanics, that is, in the basic lamina characteristics, build that up into the lamina. The design basis here is, I think, what is really needed.

I'd like to now review some of the data we have

DURABILITY WORKSHOP

II. STRUCTURAL DEVELOPMENT/QUALIFICATION PANEL

CONCLUSIONS: FLIGHT/GROUND ENVIRONMENT CAN BE DEFINED.

ADEQUATE DESIGN INFORMATION DOES NOT EXIST.

TIME/TEMPERATURE/ENVIRONMENT

FATIGUE/DEFECTS/FAILURE MODES

MORE EXTENSIVE ACCELERATED TESTING OF ELEMENTS
AND STRUCTURES REQUIRED.

ANALYSIS METHODOLOGY INCORPORATING MOISTURE
EFFECTS IS NEEDED.

generated in the lab since the time of the Battelle meeting. We have determined that moisture diffusion is described by Fick's Law and this is the work done by Springer (R-20) at the University of Michigan. We have taken pretty much all of the lamina and all of the lamina data we could collect and these are different lamina, different lay-ups, different processing conditions, different thicknesses, different resins, different fibers, and we see that the analytical prediction and the experimental data agree. Looking at the weight gain (R-21), we can see again a conclusion that the amount of moisture absorbed depends on the conditions, temperature which affects the rate of moisture absorption, and the relative humidity effects equilibrium moisture content.

A part exposed at 75 per cent humidity peaks out at a lower equilibrium moisture content than one exposed at 100 per cent relative humidity. This would ultimately reach what is termed saturation, that is, the composite would hold as much moisture as it possibly could have at the given temperature.

And I mention, remember now, that the fiber-dominated properties are not really affected by moisture, and this really is a function of the kind of test specimen you use. But here you can see that the dry notched and unnotched data and the wet data are not too different, provided you are using a test that gives you the fiber properties of the composite (R-22).

Now, thermal spiking has been the subject of a lot of testing and everyone's using a different thermal spike and it's

MOISTURE DIFFUSION IS DESCRIBED BY FICK'S LAW

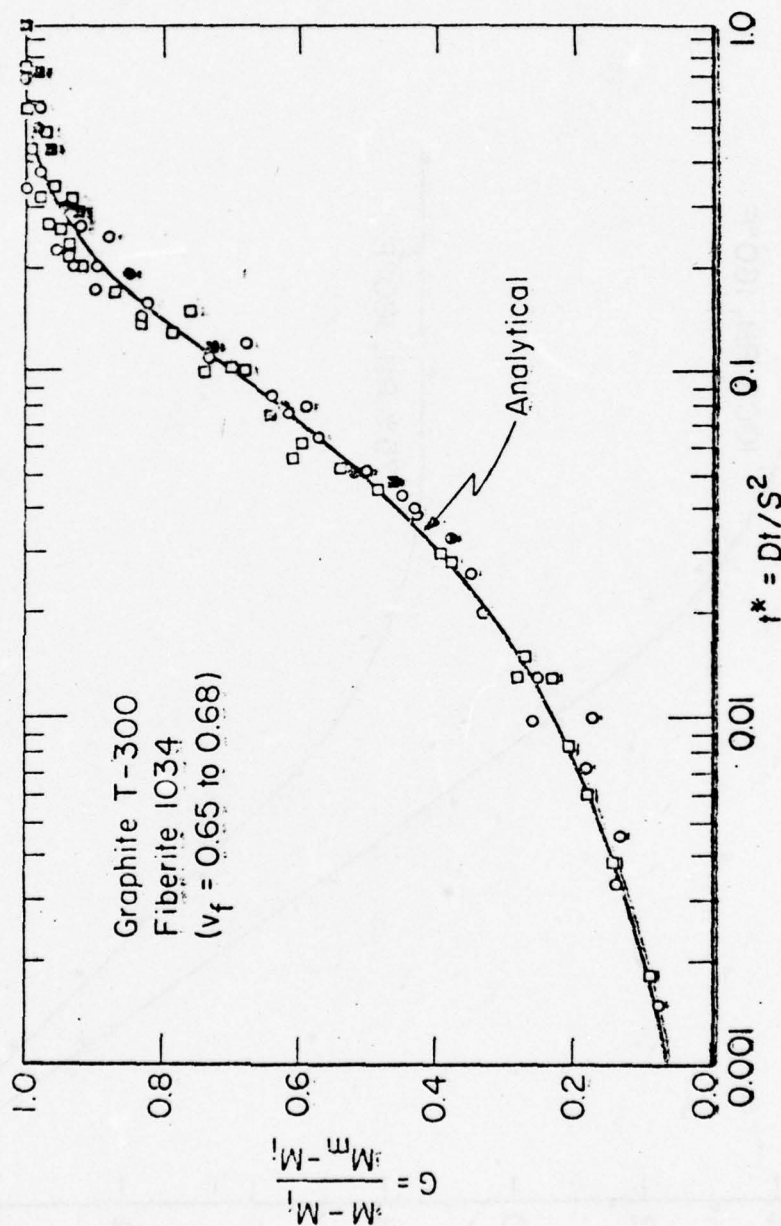
DIFFUSION EQUATION

$$\nabla \cdot (D \nabla u) = \partial u / \partial t$$

∇ GRADIENT

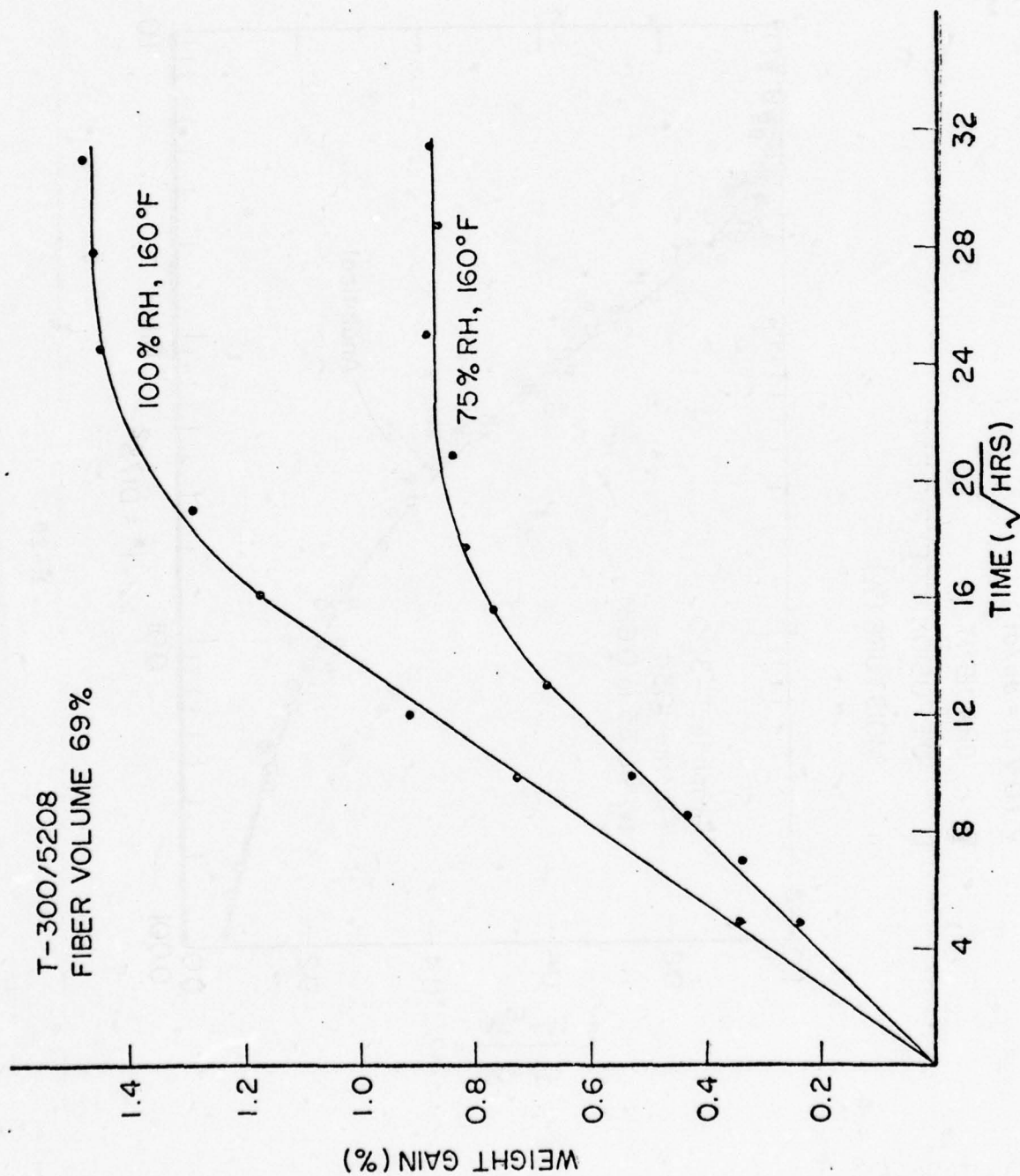
D DIFFUSION COEFFICIENT

u MOISTURE (%)



R-20

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UNIVERSITY OF DAYTON



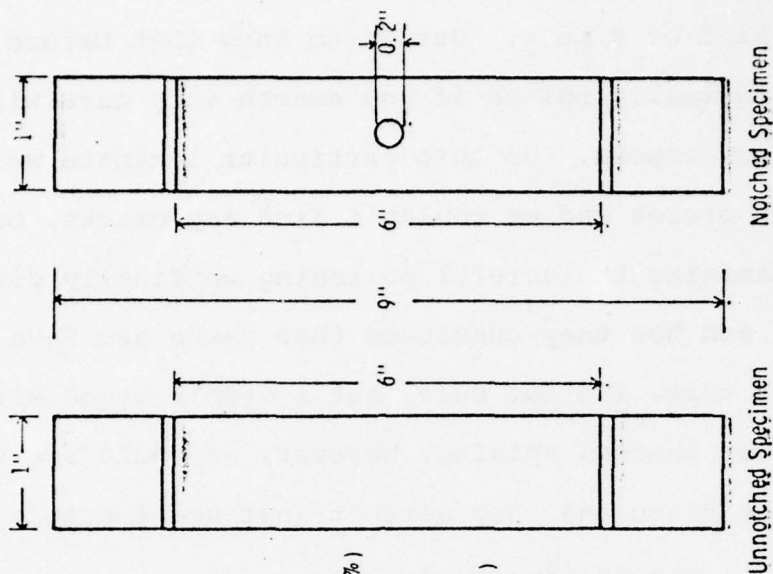
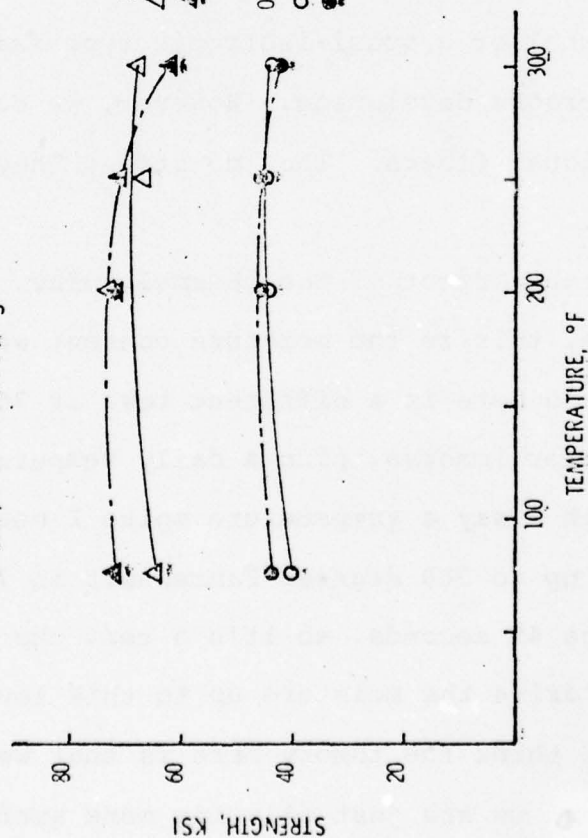
R-21

GRAPHIC ARTS SECTION
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TENSILE STRENGTH IS INSENSITIVE TO TEMPERATURE AND MOISTURE

MATERIAL: GRAPHITE/EPOXY TYPE AS / 3501

ORIENTATION: $[0/90/\pm 45]_S$



R-22

GRAPHIC ARTS SECTION
UNIVERSITY OF DAYTON

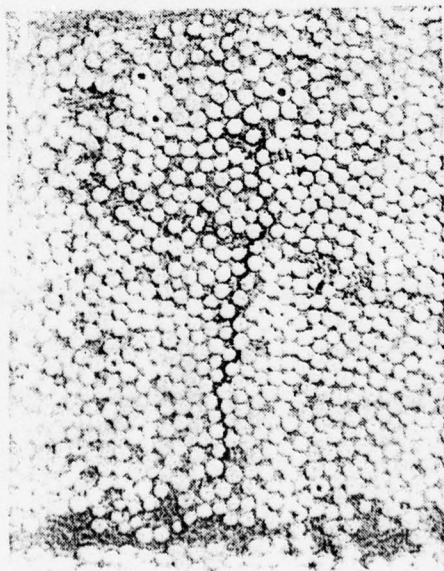
got to be kind of a mess. But we do know that before a composite is thermally spiked if you search very carefully you can find some cracks. On this particular laminate we cut up five or six pieces and we couldn't find any cracks, but with careful examining the careful polishing we finally did find one crack, and how they concluded that there are five cracks per inch in that, I'm not sure, but I didn't argue with them.

After thermal spiking, however, we could see cracks all over the place and they weren't just small cracks but they were big cracks (R-23).

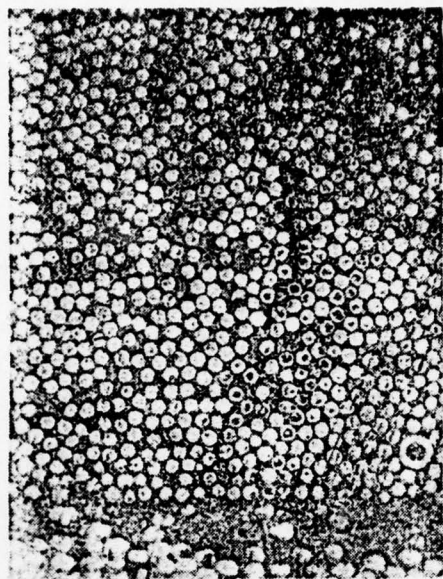
Now, another thing I should mention is that we only see the cracks in a unidirectional specimen. If we look at a bidirectional or a quasi-isotropic type lamina we do not see matrix cracks developing. However, we do see cracks between individual fibers. They do stop. They don't cross the fiber plies.

Another effect of the thermal spike, following the circle curve, this is the moisture content we get after water immersion, and here is a different test at 75° Fahrenheit (R-24). But if we water immerse, plus a daily temperature spike to 300, and when I say a temperature spike I mean probably we are getting up to 300 degrees Fahrenheit in less than a minute, maybe 45 seconds, so it's a real thermal shock, we see that we can drive the moisture up to this level under a water spike, and I think the theory here is that we are opening the cracks and we are just allowing more surface area for moisture diffusion and actually physically entrapping moisture,

SEVERE THERMAL SPIKES CAN PRODUCE MATRIX CRACKS



BEFORE THERMAL SPIKE
5 CRACKS / 1 IN.

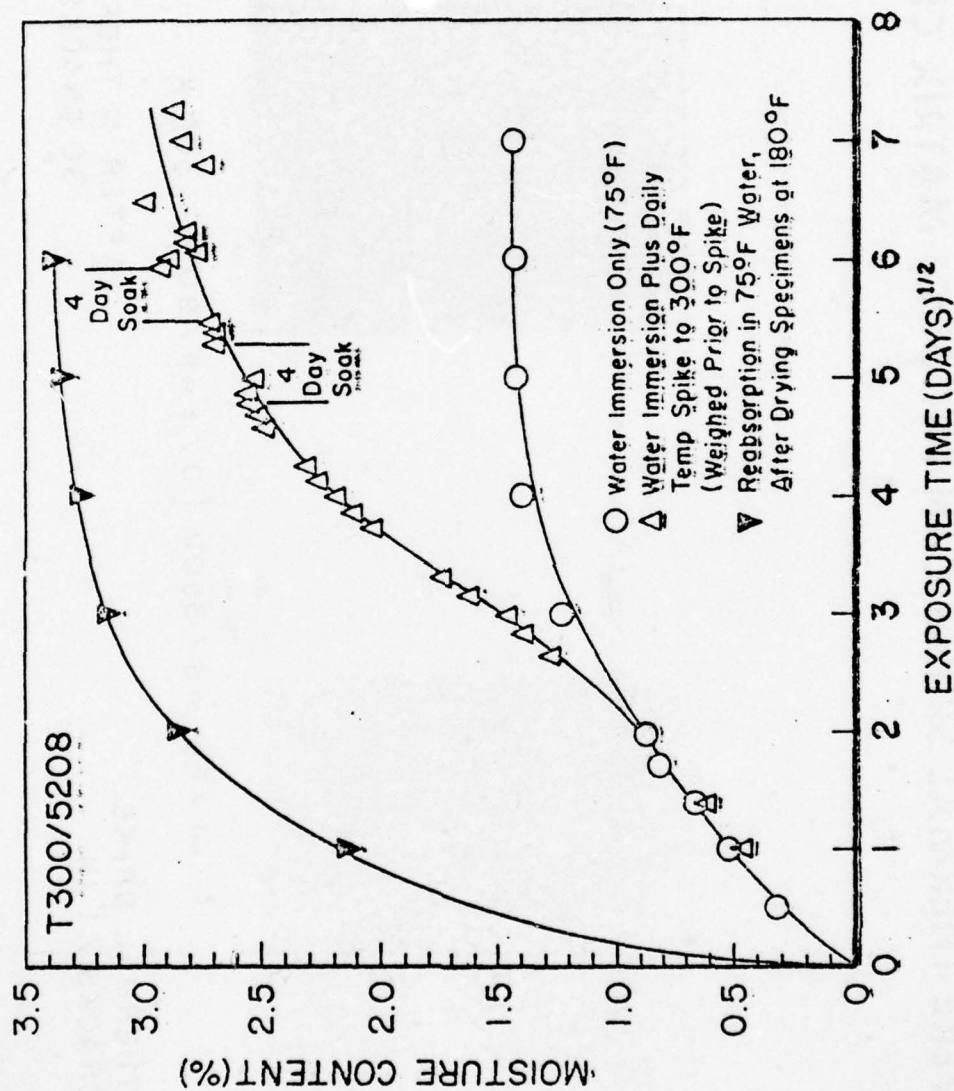


Gr / Ep AS / 3501 [0 / ± 45 / 90]_s , 300 X

AFTER 11 THERMAL SPIKES
30 CRACKS / 1 IN.

R-23

MOISTURE DIFFUSION CAN BE ALTERED BY SEVERE THERMAL SPIKES



R-24

GRAPHIC ARTS SECTION
UNIVERSITY OF DAYTON

water, liquid water in the cracks.

Now, if we dry that piece out and then expose it again to water immersion at 75°F, this is the peak we can reach with that composite.

Unfortunately, most of our aircraft that we are talking about do have a thermal spike of one kind or another. Now, this is something we are still investigating. We are not so sure we understand all the things that thermal spikes can do to us.

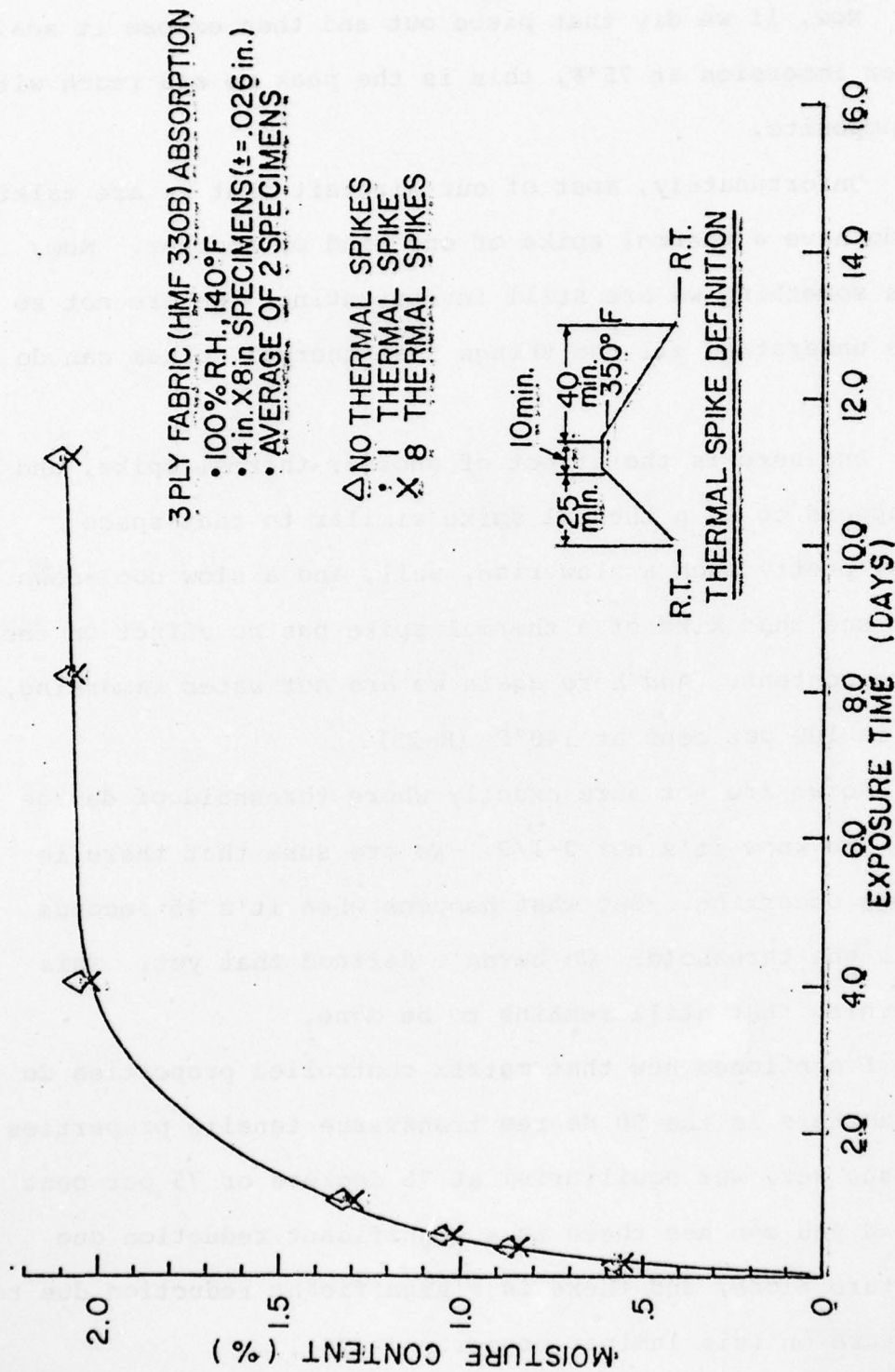
And here is the effect of another thermal spike, and this happens to be a thermal spike similar to that space shuttle, pretty much a slow rise, well, and a slow cool-down. You can see that kind of a thermal spike has no effect on the moisture content. And here again we are not water immersing, but it is 100 per cent at 140°F (R-25).

So we are not sure exactly where threshold of damage occurs. We know it's not 2-1/2. We are sure that there is no damage occurring. But what happens when it's 45 seconds where is the threshold? We haven't defined that yet. This is something that still remains to be done.

I mentioned now that matrix controlled properties do drop, and this is the 90 degree transverse tensile properties dry versus wet, wet equilibrium at 75 degrees or 75 per cent R.H., and you can see there is a significant reduction due to moisture alone, and there is a significant reduction due to temperature on this laminar property (R-26).

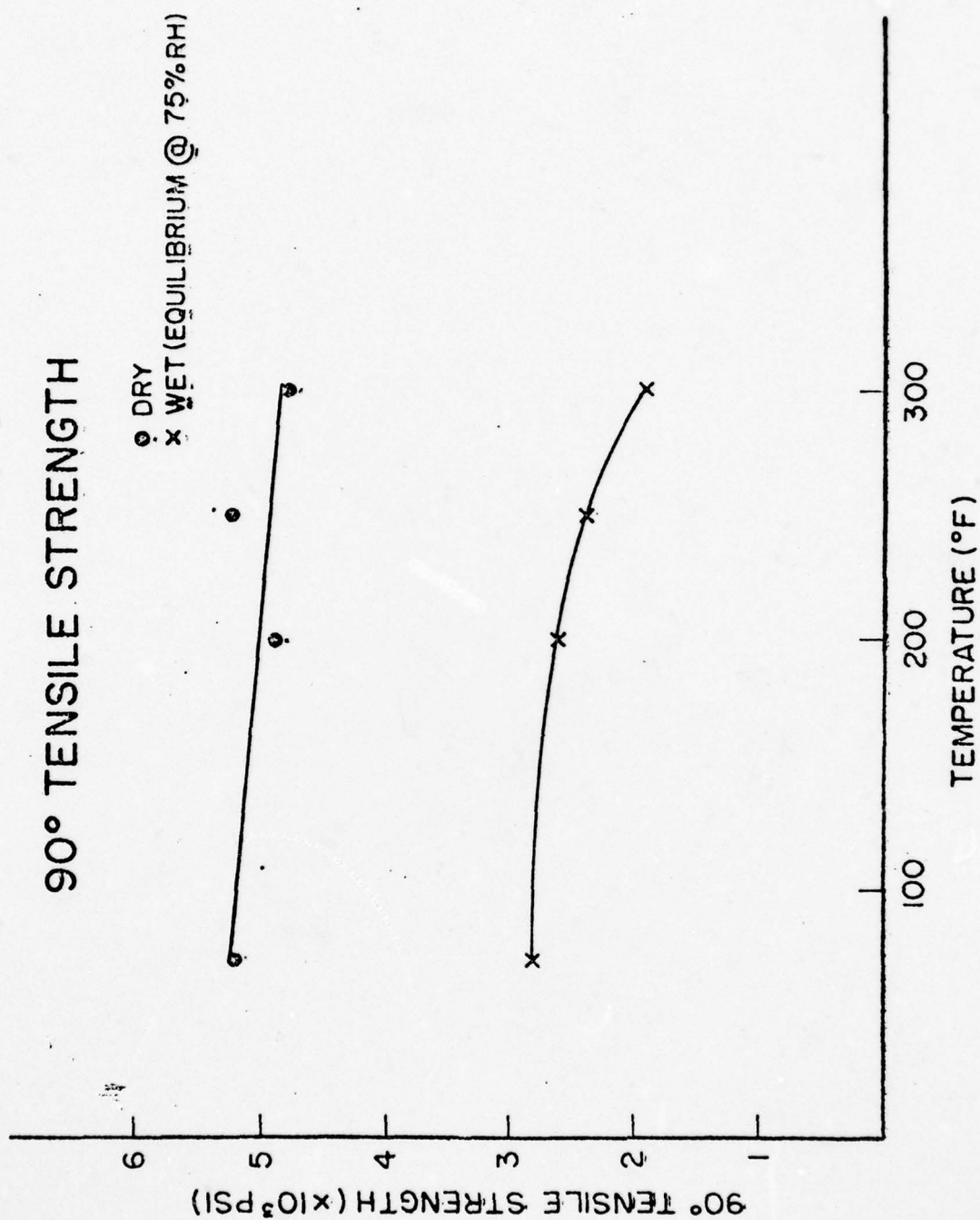
Here again in effect on the matrix-dominated (R-27)

THERMAL SPIKE DID NOT CHANGE THE READSORPTION BEHAVIOR OF T300/934 FABRIC SPECIMENS



R-25

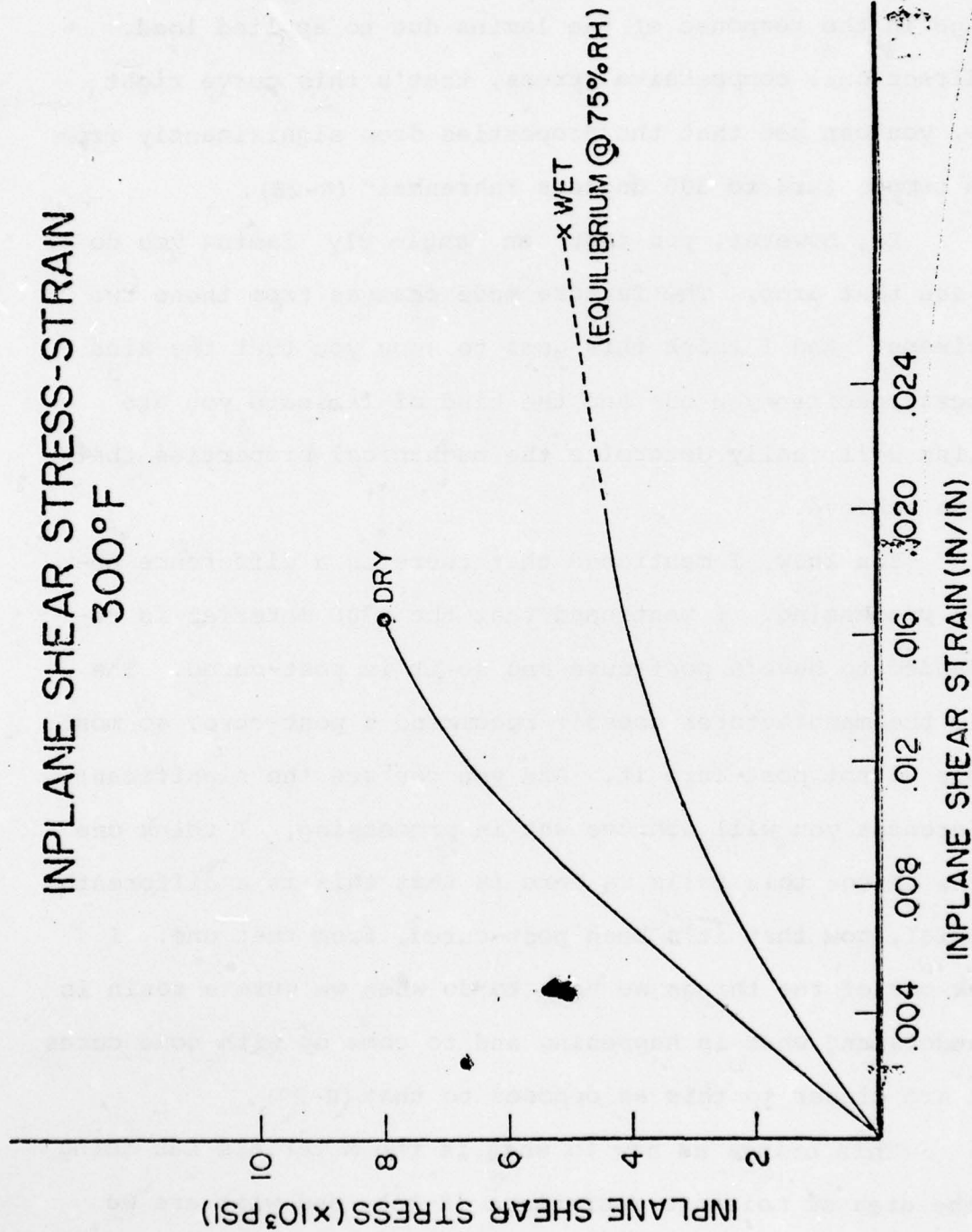
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R-26

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INPLANE SHEAR STRESS-STRAIN
300°F



R-27

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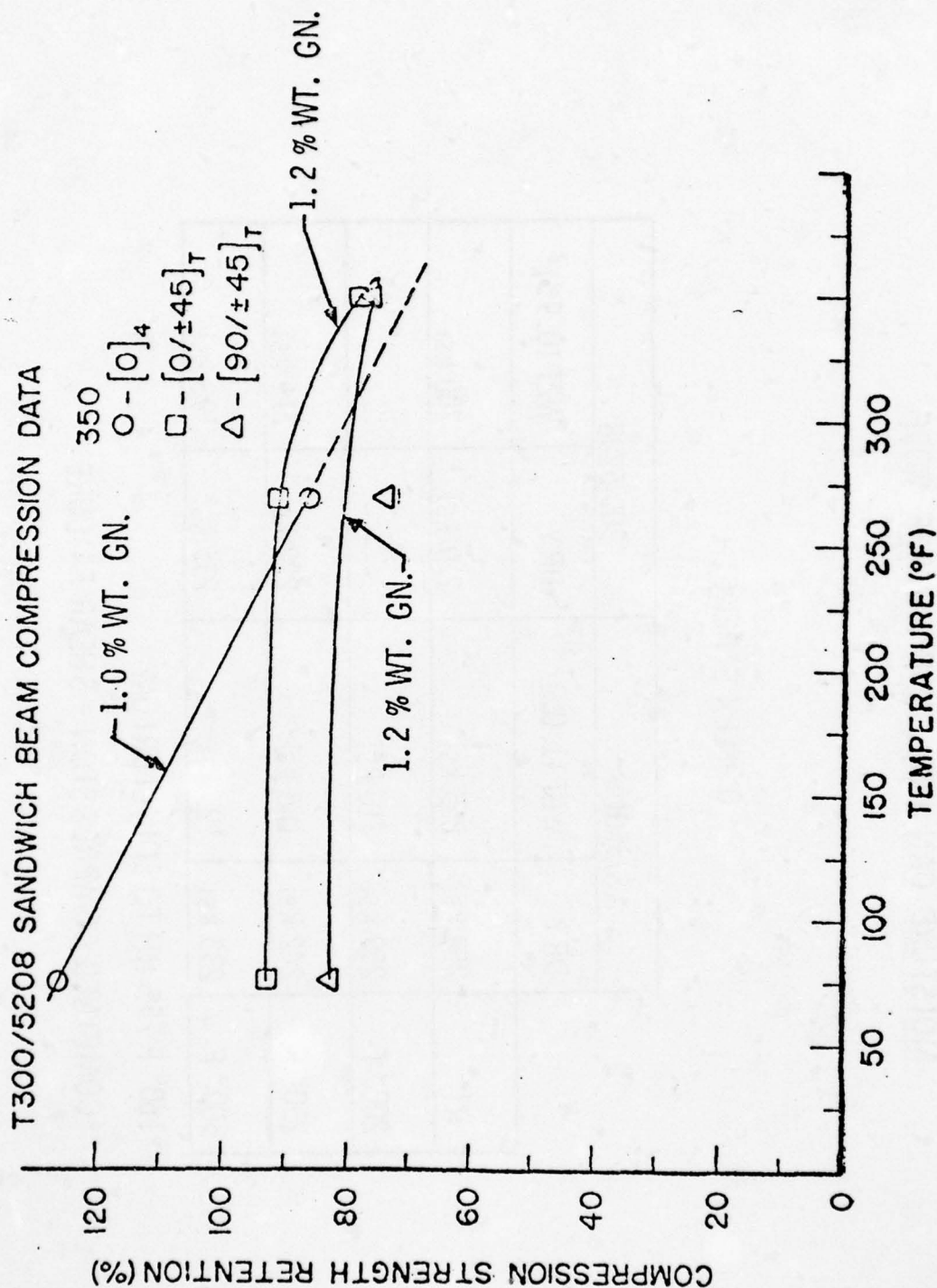
characteristics, inplane shear stress-strain at 300 degrees Fahrenheit, dry and wet, a significant reduction, a significant change in the response of the lamina due to applied load. Unidirectional compressive stress, that's this curve right here, you can see that the properties drop significantly from room temperature to 300 degrees Fahrenheit (R-28).

If, however, you test an angle ply lamina you do not see that drop. The failure mode changes from these two specimens. And I think this goes to show you that the kind of test specimen you use and the kind of laminate you are testing will really determine the mechanical properties that you do achieve.

You know, I mentioned that there is a difference between processing. I mentioned that the 5208 material is recommended to have a post-cure and so it is post-cured. The 3501, the manufacturer doesn't recommend a post-cure, so most people do not post-cure it. And you can see the significant differences you will achieve wet in processing. I think one of the things this tells us here is that this is a different material, now that it's been post-cured, from that one. I think one of the things we have to do when we cure a resin is to understand what is happening and to come up with some cures that are closer to this as opposed to that (R-29).

This brings us now to what is the Materials Lab doing in the area of moisture resistance (R-30), and what are we going to do, and when are we going to do it? We have two approaches. We have an in-house capability (R-31) in which

UNIDIRECTIONAL COMPRESSION STRENGTH DOES NOT CONVERT DIRECTLY TO LAMINATE STRENGTH



R-28

GRAPHIC ARTS SECTION
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PROCESSING IN CONJUNCTION WITH TEMPERATURE AND
MOISTURE CAN INFLUENCE FAILURE MODE

0° FLEX STRENGTH

	AS/3501		T300/5208	
	DRY	WET (1.0%)*	DRY	WET (0.9%)*
RT	259 ksi	265 ksi	229 ksi	240 ksi
200° F	259 ksi	210 ksi	-----	-----
250° F	242 ksi	166 ksi**	222 ksi	216 ksi
300° F	233 ksi	125 ksi**	236 ksi	198 ksi

*160° F 75% RH TO EQUILIBRIUM

**COMBINED COMPRESSION - SHEAR FAILURE

R-29

GRAPHIC ARTS SECTION
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PRESENT AFML PROGRAM

ACTIVITIES DIRECTED AGAINST

THE MOISTURE PROBLEM

R-30

IN-HOUSE PROGRAMS

1. DEFINITION OF MECHANISMS OF MOISTURE EFFECTS (WUDT)
MBC/MBM
2. DEVELOPMENT OF MOISTURE RESISTANT RESINS (MBC) (WUD)
3. SYNTHESIS ATQ (ATX) AROMATIC (MBP)
4. LONG-TERM DATA GENERATION B-I COMPOSITES (MXE)
5. B-I SPECIMEN FATIGUE TESTING (AFFDL)

CONTRACT PROGRAMS

1. DEVELOPMENT OF MOISTURE RESISTANT RESINS
2. DETERMINE ROLE OF INTERFACE (RESIN/FIBER)
3. NDI MOISTURE MEASUREMENT
4. DEFINITION OF CHEMICAL EFFECTS OF MOISTURE

R-31

we are doing some work to try to understand what is going on here, and we have some contract efforts. First I'd like to cover the in-house. (R-32), (R-33) We have a program being headed up by Dr. Charles Browning in the Lab to try to determine the specific mechanisms by which moisture degrades the epoxies. (R-34) He is looking at such things as the binding energy of the moisture to the hydroxyl groups, to the ether linkages, and he is trying to determine really what is the mechanism of this attack. He is not looking at the chemistry now but strictly the physical mechanisms of what water does. And, hopefully, once we understand this, there will be some obvious approaches, and I'm not holding my breath on that, to combat the moisture problem.

We have in-house programs to develop moisture resistant resins. (R-35) This is a short-term program looking at various epoxies, various other resins, trying to shield the active groups that we think are picking up the moisture, trying to eliminate them from the resins.

Various approaches have been tried here as a short-term answer to the moisture problem. We don't have great hope there, either. That's kind of a high-risk problem. The polymer branch is working on aromatic polymers. (R-36) One of the approaches they have is by tacking on acetylene groups as chain terminations. We find that we can thermally polymerize these acetylene groups and come up with good cross-linked resins that don't have the water attractive groups that the epoxies and some of the polyimids have. Hopefully,

MOISTURE RESISTANCE OF COMPOSITES

IN-HOUSE PROGRAMS

1. DEFINITION OF MECHANISMS OF MOISTURE EFFECTS (WUD)
MBC/MBM
2. DEVELOPMENT OF MOISTURE RESISTANT RESINS (WUD)
MBC
3. SYNTHESIS ATQ (ATX) AROMATIC RESINS (WUD)
MBP
4. LONG-TERM DATA GENERATION (B-I) COMPOSITES
MXE
5. B-I SPECIMEN FATIGUE TESTING
AFFDL

R-32

AD-A035 437

DELAWARE UNIV NEWARK CENTER FOR COMPOSITE MATERIALS

F/G 11/4

THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED TEMPERATURE ON CO--ETC(U)

DEC 76 J R VINSON, R B PIPES, W J WALKER

AF-AFOSR-2966-76

UNCLASSIFIED

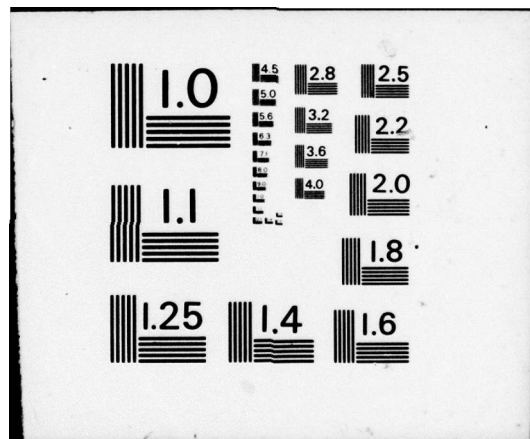
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2 of 6

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IN-HOUSE PROGRAM (A)

I. DEFINITION OF MECHANISMS OF MOISTURE EFFECTS

OBJECTIVE:

- a. TO DETERMINE THE EFFECT OF ENVIRONMENT ON THE MECHANICAL PROPERTIES OF COMPOSITES.
- b. TO DEVELOP A PRACTICAL, ANALYTICAL PROPERTIES PREDICTION CAPABILITY.

APPROACH:

GENERATE BASIC PLY DATA AS WELL AS COMPOSITE PROPERTIES SUCH AS TENSION, COMPRESSION, SHEAR UNDER EQUILIBRIUM MOISTURE CONDITIONS AT VARIOUS TEMPERATURES ON AS/3501 AND T300/5208.

TESTING INCLUDED T_g DETERMINATIONS AS WELL AS THERMAL SPIKE EFFECTS.

PROJECT ENGINEER: J. WHITNEY
G. HUSMAN

IN-HOUSE PROGRAM (B)

I. DEFINITION OF MECHANISMS OF MOISTURE EFFECTS

OBJECTIVE:

DETERMINE CHEMICAL/PHYSICAL MECHANISMS OPERATING IN THE MOISTURE DEGRADATION OF EPOXY RESINS.

DETERMINE PHYSICAL/MECHANICAL BEHAVIOR OF EPOXY RESINS AND COMPOSITES AS A FUNCTION OF ABSORBED MOISTURE.

APPROACH:

5208 AND 3501 MATRIX RESINS ARE BEING STUDIED TO DETERMINE IF MOISTURE CAUSES CHEMICAL CHANGES IN RESIN. STRESS RELAXATION AND DYNAMIC PROPERTIES ARE BEING MEASURED FOR VARIOUS FORMULATIONS AND PROCESSING CONDITIONS.

ATTEMPTS ARE BEING MADE TO DETERMINE LOCATION OF MOISTURE ATTACK AND ITS BONDING ENERGY IN THE EPOXY MATRIX MATERIAL.

PROJECT ENGINEER: C. E. BROWNING

R-34

IN-HOUSE PROGRAM

2. DEVELOPMENT OF MOISTURE RESISTANT RESINS

OBJECTIVE:

THE DEVELOPMENT OF TOUGH, MOISTURE RESISTANT RESINS WHICH ARE EASILY PROCESSED AND HAVE LONG STORAGE LIFE.

APPROACH:

CHEMICAL MODIFICATION OF EXISTING HIGHLY THERMAL, STABLE AND MOISTURE RESISTANT BASE POLYMERS TO PRODUCE ACETYLENE TERMINATED MATERIALS WHICH CROSSLINK THROUGH ADDITION.

PROJECT ENGINEER: L. G. PICKLESIMER

R-35

IN-HOUSE PROGRAM

3. SYNTHESIS OF ACETYLENE TERMINATED POLYMERS

OBJECTIVE:

TO DEVELOP NEW POLYMERIC MATERIALS FOR COMPOSITES AND ADHESIVES HAVING SIGNIFICANTLY IMPROVED RESISTANCE TO HEAT AND HUMIDITY AND EPOXY-LIKE PROCESSABILITY.

APPROACH:

ACETYLENE TERMINATIONS WILL BE ADDED TO NEW MONOMERS AND OLIGOMERS SYNTHESIZED TO HAVE THE SPECIFIC CHARACTERISTICS OF HEAT AND HUMIDITY RESISTANCE, LOW VISCOSITY, TOUGHNESS AND GOOD ADHESION.

PROJECT ENGINEER: F. ARNOLD (MBP)

R-36

this approach will give us modestly moisture resistant, easy coring materials. They certainly won't cure in the same ballpark as the epoxies, but they should have fantastically better moisture resistance and good processing, like good flow, long out time, and low void content.

Another program (R-37) we have going in-house is a long-term data generating program using specifically the B-1 thermal cycle, and this is going to be, I hope, a five-year program where we will expose small and large specimens to stress and accelerated aging to determine how bad off are we after five years. Periodically then we would pull out specimens, say, every three to six months, give them fatigue cycles, put them back, or test them for residual strength.

There is a program going on in the Flight Dynamics Lab and I wanted to mention that. We are exposing some large specimens purchased from Grumman for the Flight Dynamics people. Their approach here will be to give these specimens two lifetimes of the fatigue cycles, and I'm not sure that they have selected the fatigue cycle yet but it probably will approximate the B-1 flight spectrum. The fatigue testing will be done under conditions of aggressive environment, the temperature spike and all that. After the two lifetimes of fatigue, they will be tested for residual strength.

We have about 25 of these specimens so we should have pretty good indications of what is going on here.

In our contract program we have a program to develop new moisture resistant resins (R-38). We have one coming out

IN-HOUSE PROGRAM (AFFDL)

5. B-1 SPECIMEN FATIGUE TESTING

OBJECTIVE:

TO DETERMINE RESIDUAL STRENGTH OF COMPOSITES
AFTER EXPOSURE TO HEAT/HUMIDITY AND FATIGUE
LOADING.

APPROACH:

SPECIMENS WILL BE ENVIRONMENTALLY CONDITIONED
TO MOISTURE SATURATION. FATIGUE CYCLING
(UNDER ENVIRONMENT) UP TO TWO LIFETIMES WILL
BE IMPOSED. SPECIMENS WILL SUBSEQUENTLY
BE TESTED STATICALLY TO DETERMINE RESIDUAL
STRENGTH.

PROJECT ENGINEER: D. SHIRRELL

R-37

MOISTURE RESISTANCE OF COMPOSITES

CONTRACT PROGRAM

I. DEVELOPMENT OF MOISTURE RESISTANT RESINS

OBJECTIVE: TO DEVELOP A HYSTIL MODIFIED EPOXY (HME) RESIN SUITABLE FOR USE AT 350°F SERVICE TEMPERATURES.

TO RETAIN LOW-FLOW, LOW-PRESSURE CURE CAPABILITIES.

TO EXPLORE OTHER APPROACHES TO PRODUCING MOISTURE RESISTANT RESINS.

APPROACH:

DEVELOP AND EVALUATE RESIN FORMULATIONS BASED ON MODIFIED HIGH VINYL POLYBUTADIENE POLYMERS.
EVALUATE COMPOSITES FABRICATED FROM HOT-MELT-COATED PREPREG.

CONSIDERED OTHER RESIN APPROACHES INVOLVING ACETYLENE TERMINATED MONOMERS/OLIGOMERS HAVING POTENTIAL FOR RESISTANCE TO MOISTURE.

PROJECT ENGINEER: C. BROWNING

in the fiscal year '77; hopefully, fiscal year '78 will have one or two more. These are long-range programs. It's not anticipated that we will come up with an answer in one year or two years. The problem is much more difficult than that.

We will have a program to determine the interface problem. (R-29) What we'd like to do is find out what does moisture do at the interface. We know it must be a reversible or a mechanical effect because we can get interface properties back upon drying out. One of the things we'd like to do here is to build a more durable interface. We don't necessarily need a stronger one. The interlaminar shear properties we are achieving now in our composites are more than adequate for most applications, but what we'd like to stop is the properties depressing effect of moisture.

Another program is trying to define a technique for the NDI, Non-Destructive Inspection of moisture. (R-30) We have a part sitting on the runway and it has a protective coating, its lightning protection, and all the other things that have to go on a composite part on an airplane, how do we determine the moisture content of that part?

I'm not really holding my breath on this one either. That's a tough job. I don't know how they are going to attack it.

We also have a program with Ram Levy, I don't know if he is here today, at McDonnell-Douglas, to define the chemical effects of moisture attack. (R-31) Ivan Goldfarb is the project engineer on this, and maybe he will talk about

MOISTURE RESISTANCE OF COMPOSITES

CONTRACT PROGRAM

2. DETERMINE ROLE OF INTERFACE (RESIN/FIBER)

OBJECTIVE: TO DETERMINE THE CHEMICAL/PHYSICAL MECHANISMS OPERATING TO CAUSE DEGRADATION AT THE FIBER RESIN INTERFACE.

TO DEVELOP APPROACHES TO MINIMIZE INTERFACE DEGRADATION DUE TO THE ABSORPTION OF MOISTURE.

APPROACH: DETERMINE USING INSTRUMENTAL ANALYTICAL TECHNIQUES; THE NATURE OF THE DEGRADATION MECHANISMS TAKING PLACE AT THE INTERFACE DUE TO ABSORBED MOISTURE.

MINIMIZE DEGRADATION THROUGH APPLICABLE CHEMICAL OR PHYSICAL METHODS DEPENDING ON NATURE OF DEGRADATION REACTION.

PROJECT ENGINEER: L. DRZAL

MOISTURE RESISTANCE OF COMPOSITES

CONTRACT PROGRAM

3. NDI TECHNIQUE FOR MOISTURE MEASUREMENT

OBJECTIVE: TO DEVELOP A FIELD NDI TECHNIQUE FOR THE MEASUREMENT OF MOISTURE IN COMPOSITE COMPONENTS.

APPROACH: CONVENTIONAL ELECTRONIC (MICROWAVE, CONDUCTIVITY) TECHNIQUES WILL BE EVALUATED FOR APPLICABILITY AND EFFECTIVENESS.

THE FEASIBILITY OF THE USE OF BUILT-IN SENSORS TO DETECT ABSORBED MOISTURE WILL BE DETERMINED.

MOISTURE RESISTANCE OF COMPOSITES

CONTRACT PROGRAM

4. DEFINITION OF CHEMICAL EFFECTS OF MOISTURE

OBJECTIVE: TO DETERMINE THE CHEMICAL MECHANISMS
OPERATING IN THE DEGRADATION OF EPOXY RESINS.

APPROACH: STUDY VIA MECHANICAL TEST AND INSTRUMENTAL
ANALYSIS THE MECHANICAL AND CHEMICAL EFFECTS
PRODUCED IN EPOXY RESINS BY ABSORBED MOISTURE.

PROJECT ENGINEER: I. GOLDFARB

R-41

it a little bit in his session. I guess the results to date show that they find little evidence of chemical degradation of the resin due to moisture

I think I'd just like to summarize the kinds of things that we think we have learned since the Battelle meeting.

Number one, very obviously, equilibrium amounts of water are proportional to the relative humidity that you have exposed the part to. One of the things we have not defined yet is in our accelerated testing. Are getting a significantly different distribution of moisture in the composite than we do at real time testing? How does this affect mechanical properties? Is the fatigue data that we are going to generate using accelerated testing meaningful to the real life application?

Highest value of saturation at 100 per cent that we have seen, now, this is a neat epoxy resin, is 7 per cent. And this is after thermal spiking. That's pretty high. That's a number that's very, very high. We will ignore these two because we have talked about that before. That's not too surprising, either, that the composite diffusivity should be pretty much the same as the resin diffusivity.

Activation energies for diffusion are lower for composites than for resins. That's also not too surprising.

Thermal spiking increases the rate and amount of moisture absorbed, and I think this is just an area problem due to the amount of cracking in the composites. Our measurements show that the resin swells linearly with absorbed moisture.

What influence this has on the composite design, we don't know at this time.

And the last one I have talked about, concentration gradients, this is in the area that we are going to have to do more work to determine if the concentration gradient seriously affects our mechanical properties. I believe that is all.

I think, really, what we are looking for from this group in the next couple of days is, as I mentioned, everyone is off doing their own thing. I think we would like, personally I would like some real strong guidelines as to recommendations for accelerated testing. How do we come up with a standard test so we can compare data between all of the groups that are working in the moisture resistant problem?

Thank you.

DR. PIPES: Thank you, Ted.

Our first industrial program speaker is Mr. Max Waddoups of the General Dynamics Corporation, Fort Worth, Texas.

2. Industrial Programs

MR. WADDOUPS: I have a few simple points to make. My reason for being here today is to talk to you about our application for composites and our attitude towards the technical issue of moisture.

In the development of composites, you might think from reading the literature there has been a painstaking, careful, scientific effort with very few problems. I want to relate to you a few of the technical issues I have seen in the short time I have been involved in the business.

My first one occurred when Hercules was trying to commit Minuteman II to production. On about the 6th qualification motor case, the tensile burst pressure dropped about 50 per cent. Six months were spent attacking materials problems in terms of interface and resin changes. At the end of the nine months when we were about to not qualify the case we corrected a simple design deficiency, it went into production and they have been very serviceable motors since that time.

My first point to make is that it was not a very simple problem and in fact it involved a design deficiency.

In advanced composites the first resin we used required hand lay-up using 1/8th inch tape in a freezer. We inherited a resin from the rocket motor industry and it was simply a mess to handle. We went into our second generation of resins on boron epoxy and developed more processable systems. We tried to scale boron into production. At the time we were working on an F-111 horizontal tail and our competitors were looking at new airplanes.

The first thing that happened when the fiber went into production, scaling up from the laboratory fiber, was the tensile strength dropped 40 per cent and we were left without material for six months. In the development of graphite, we went down the blind alley furnished by the British. The initial emphasis was expended developing Type I graphites which were unacceptable as aircraft structural materials. We made a major commitment to graphite epoxy for the YF-16 empennage, the first airplane components using graphite epoxy primary structure. One month after making the commitment and talking to the chief engineer about the wonderful things we were going to do for him, the scale-up of Type II graphite for meter length material to continuous length material resulted in a 30 per cent loss of tensile strength. We started that program with no material, (W-1).

And now we are on the eve of F-16 qualification, and I mean qualification, not certification. We are qualifying our first limited production run of the airplane, and we have a moisture issue.

So I am going to be cavalier about it. I'm getting a lot of gray hair out of this and every time we make an advance we have a minor set-back. In my 12-year career of observing these problems the response time to the solution is in the neighborhood of six to nine months, and that is what we are looking for now. We have some promise of getting to some reduced moisture sensitivity systems in that time period by some scientists who are really vigorously attacking the problem.

FOCUS ON GRAPHITE-EPOXY FOR THE F-16



VF-16
10-10-80

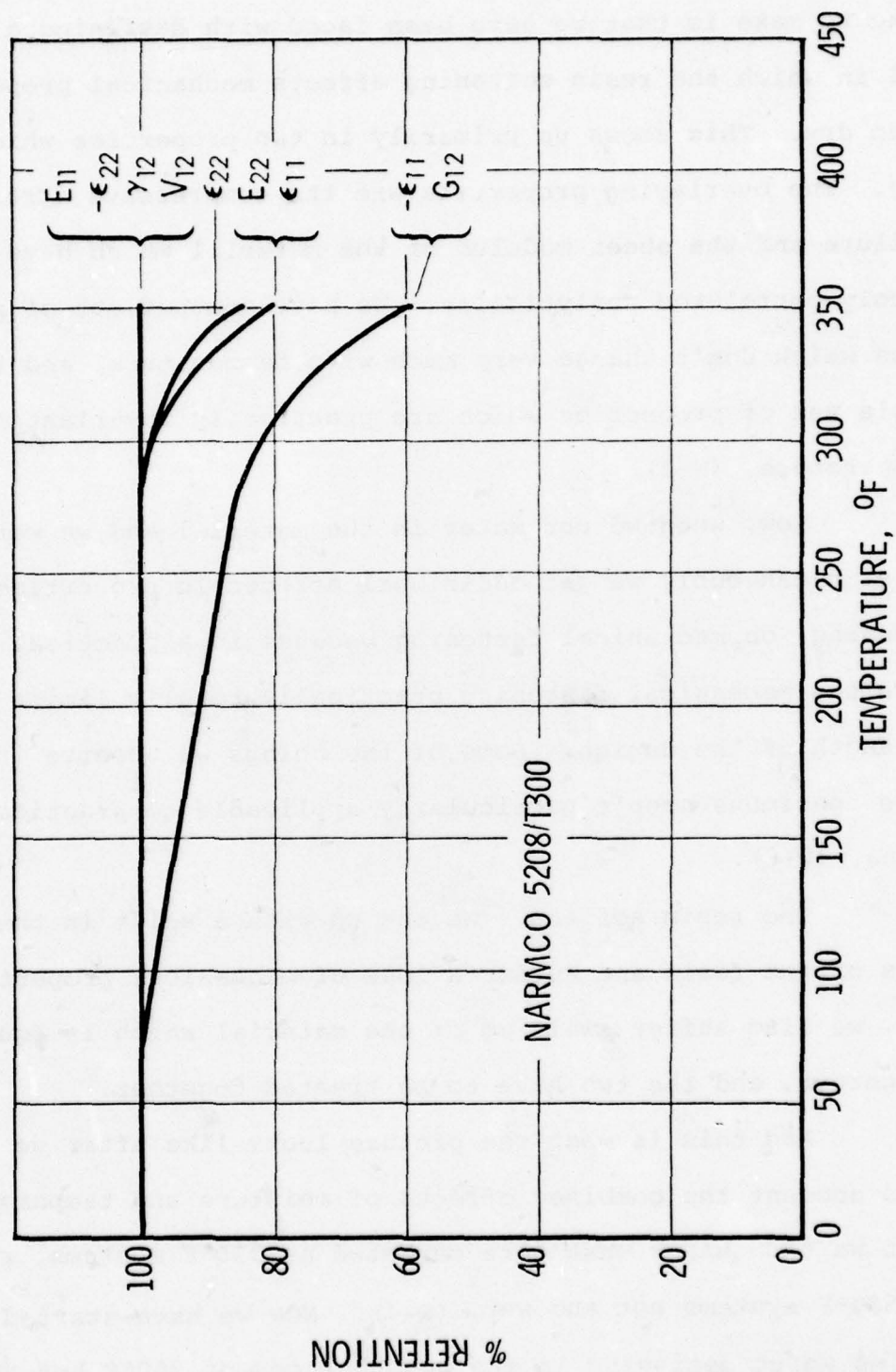
Let's just briefly review the problem. First point I'd like to make is that we have been faced with designing a material in which the resin softening effects mechanical properties even dry. This shows up primarily in two properties which overlay. The overlaying properties are the compressive strain to failure and the shear modulus of the material which have been nicely correlated analytically. We have another set of properties which don't change very much with temperature, and then a whole set of properties which are practically invariant to temperature, (W-2)

Now, when we put water in the material and we warm it up simultaneously we get additional effects in properties. I am focusing on mechanical fastening because in a practical structure the mechanical fastening practically totally limits the strength of the design. Some of the things we observe in coupon type specimens aren't particularly applicable to practical designs, (W-3).

The resin softens. We end up with a shift in the stiffness of the resin and suffer a loss of mechanical properties. Now, we also suffer swelling of the material which is equally dangerous, and the two have to be treated together.

And this is what the picture looks like after we take into account the combined effects of moisture and temperature, what we thought, or what were marketed as 350°F systems, reduced to 300°F systems hot and wet, (W-4). Now we have started having qualms about designing in the neighborhood of 250°F hot and wet.

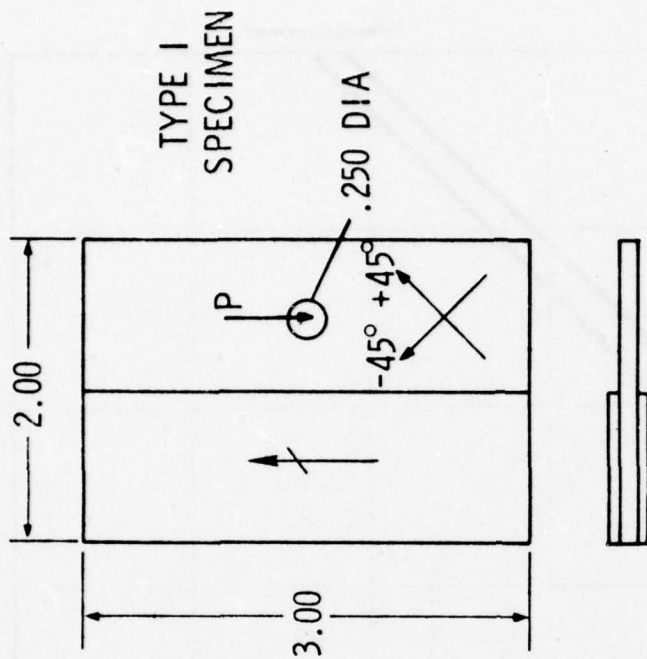
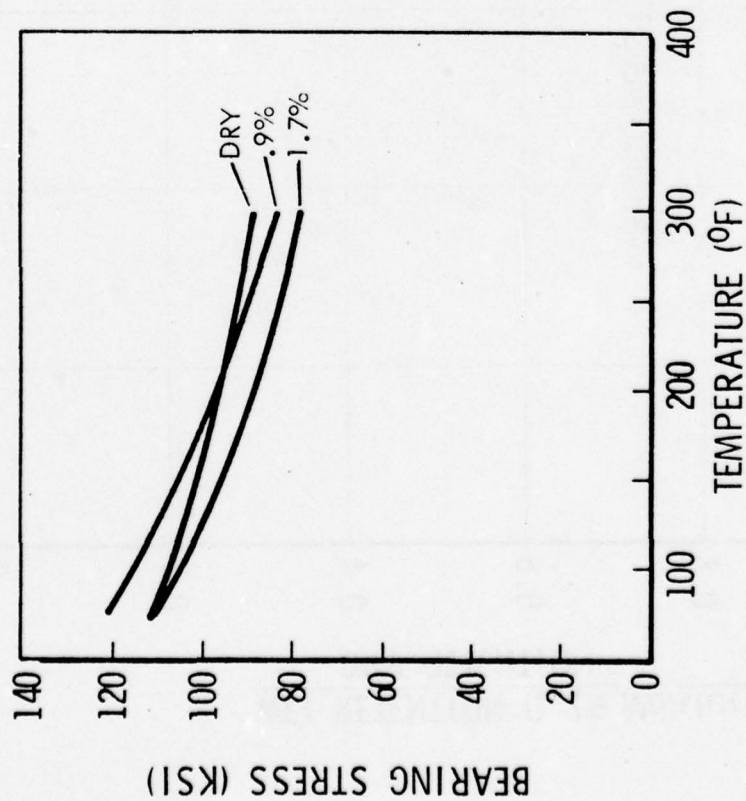
ALLOWABLES REFLECT TEMPERATURE DEPENDENCE



W-2

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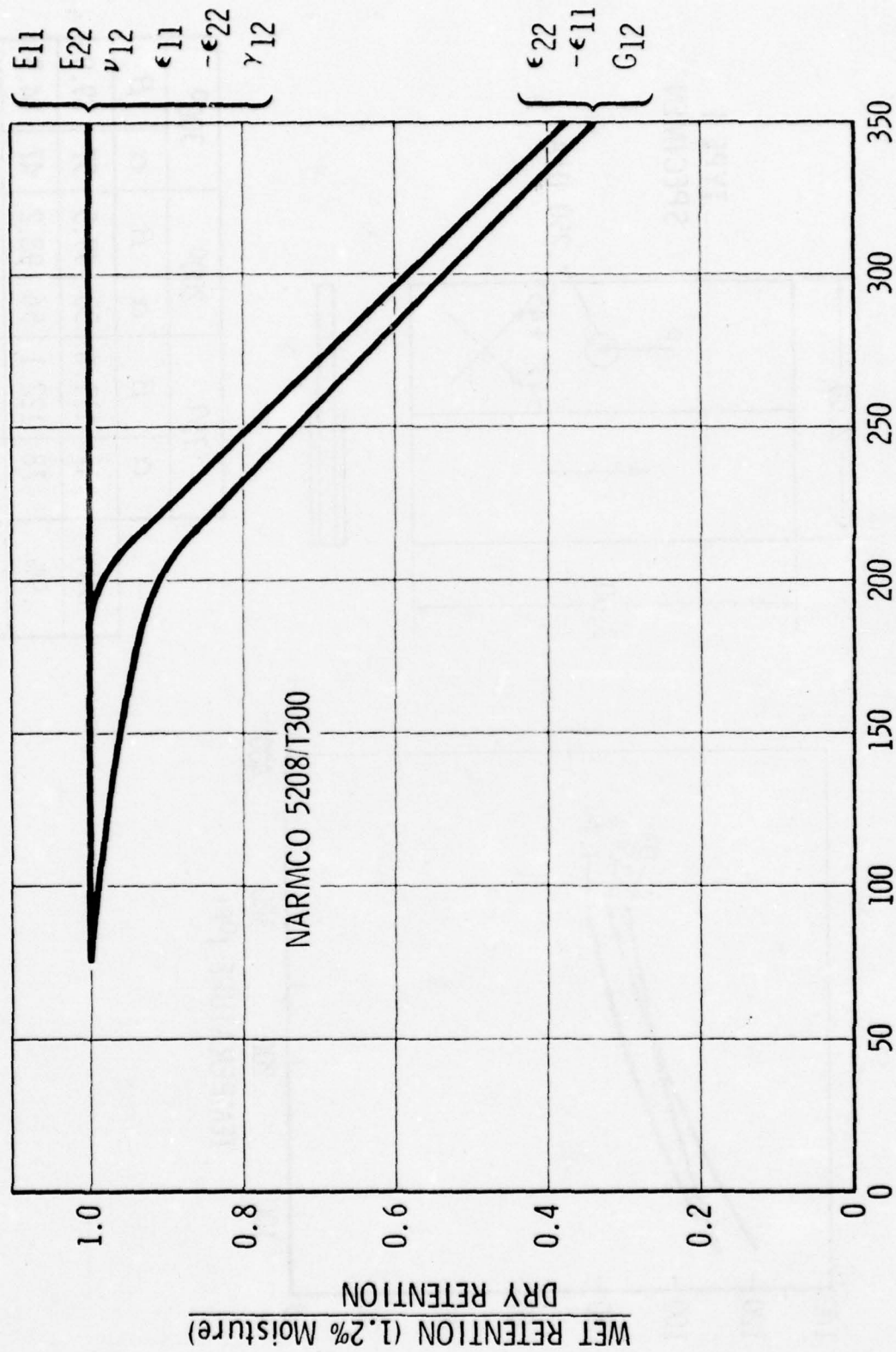
[± 45] BEARING RETENTION



	75°		200°		300°	
	α	β	α	β	α	β
DRY	47	111.6	30	99.5	57	89.9
.9%	78	122.1	56	98.2	47	84.3
1.7%	30	113.1	24	89.4	29	79.9

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26 SEPT. 1975

MOISTURE EFFECTS SOME PROPERTIES AT ELEVATED TEMPERATURE



So we have had a general trend downward in the properties as a function of environment. We have tracked the failure modes statistically in our characterizations, and as long as the materials remain a glass, which is in about the 250 degree range, our statistics and our allowables apply very nicely, so we are not having a problem there, (W-5).

Now, the other issue we are having is focusing on the failure mode. There were a few heretics running around the country in the late sixties saying all these materials fail due to pre-existing flaws and these pre-existing flaws grow in a manner to reduce the strength of the material. It was kind of an unpopular point of view because most people were looking for thresholds and stress levels at which nothing happens. But we have gotten to the point we are more comfortable with composites doing a finite life design.

I wanted to point out on this chart that our early efforts were motivated by our experience in metals, and we worked the devil out of the problems of tension, stress concentration and fatigue. We rarely produced a tension dominated fatigue flow failure in composites even in our laboratory and in our full-scale structural simulators. What we learned was that in a bonded joint, which was the first significant system studied, was that we could really look at the kinetics of the fracture process, that we did in fact have significant sub-critical growth and possible failure, (W-6).

So our first attention went to characterizing a bonded joint. In the bonded joint the moisture and temperature aspects

COMPOSITE FAILURE MODES

AMBIENT ENVIRONMENT - REALISTIC LOADS

ELEMENT	STRENGTH (Delivered Strength)	DAMAGE TOLERANCE (Residual Strength Loss)	DURABILITY (Limit Strength - Finite Life)
$\pi/4$ LAMINATE ✓Tension ✓Compression	• Brittle Fracture	• Very Slow Subcritical Flaw Growth	• Growth to Failure Rare
	• Micro Instability	• Subcritical Flaw Growth	• Failure Possible
	• Delamination	• Subcritical Flaw Growth	• Failure Possible
(±45°)s LAMINATE ✓Tension ✓Compression	• Brittle Fracture	• Subcritical Flaw Growth	• Failure Possible
	• Yield	• Subcritical Flaw Growth	• Failure Possible
BOLTED JOINT ✓Tension ✓Compression	• Brittle Fracture	• Slow Subcritical Growth	• Growth to Failure Rare
	• Bruising & Wear	• Subcritical Growth	• Failure Possible
BONDED JOINT ✓Tension & Compression	• Brittle Fracture	• Subcritical Growth	• Failure Possible

W-5

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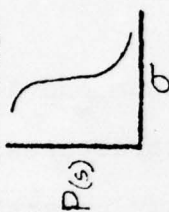
QUALIFICATION PROGRAM

• BASIC BACK-UP

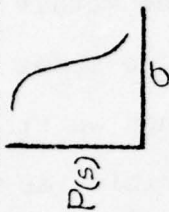
STATISTICS

ENVIRONMENT

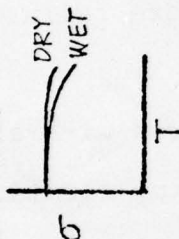
ALLOWABLES



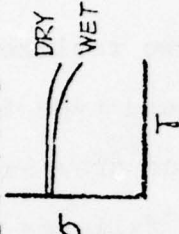
ACCEPTANCE



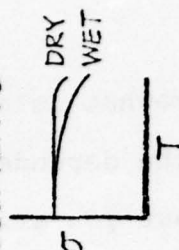
LAMINA



LAMINATE



ELEMENTS

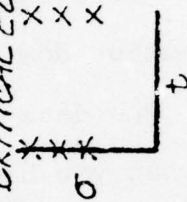


CRITICAL ELEMENTS

SCREENING

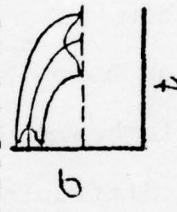
ENVIR.

FATIGUE



• DESIGN VERIFICATION

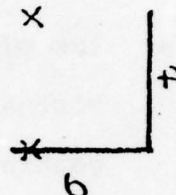
ACCELERATED



QUASI-REAL TIME



• QUALIFICATION SUPPORT



• FULL SCALE DEMONSTRATION

accelerate fatigue processes. Somewhat later it was determined that also in compression, due to the dependence of compression strength on G_{12} of the laminate that you also get microcracking and progressive breakdown of material in compression.

So five or six years ago, we realized the metals problem of fracture and tension dominated type failure modes was virtually eliminated. The data base grew and when we started getting failures and when you have failures possible, as an aircraft engineer you recognize those failures and learn how to control them.

You have the similar failures with aluminum and I have very little heartburn about designing aluminum structures. I have more difficulty with this material because my understanding isn't quite as good.

Now, this issue of moisture has also caused us another problem, and that is we have got to do a lot of testing. I'm going to give you a very candid opinion that I think a great deal of this testing might be wasted. The testing is going on to support hardware commitments and I think we ought to go as rapidly as possible to closing those commitments. In very high strength metals steels, for which we have had significant design experience, we invested a great deal of money in characterization D-6AC steel for which we developed huge data base (we knew about crack growth in sump tank water, distilled water, JP-4, process zone interactions on crack growth, and retardation), resulted in volumes of data. What did we do when we got all that data accumu-

lated? We took a look and said, "That 10 nickel steel really looks good, gets cracks 10 inches long in it before it breaks". So all that data goes dribbling down the drain.

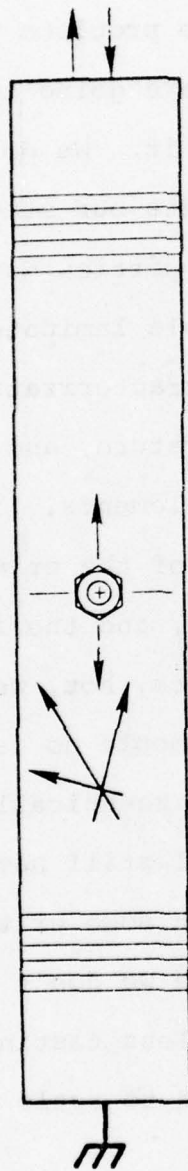
So I'm advocating get our hardware problems solved but let's not go off the deep end and say we are going to catalog a data basis for posterity and then not use it. We do our qualification using very simple tests. We accumulate our statistics on flexure specimens because we know the properties determined transfer to the fracture processes on simple laminates and laminates with discontinuities. We do characterization of wet and dry properties as a function of temperature, and then we go directly to characterization of critical elements, (W-7).

I am going to show you the impact of the critical element on a design program for real hardware, and the impact is we have to consider some pretty elaborate tests, hot, wet, and quasi real time. What I would like to see you people do is just erase this moisture problem for us, I think it's technically feasible to get a moisture resistant resin. We will still have to look at hot and wet properties and may have to test some critical conditions for the first few times just to prove we don't have something else wrong with the resin. But we can do less testing. And I think this is advantageous, because we need to scale a technology up, (W-8).

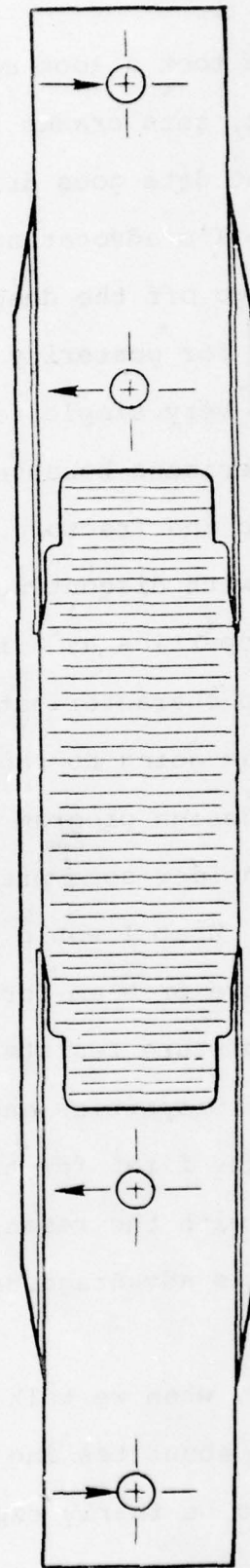
Now, when we talk about testing hot, wet, real time we are talking about testing major sub-elements on the airplane. These get to be fairly expensive tests, which include both far

QUALIFICATION SUPPORT SPECIMENS

● VERTICAL FIN



● HORIZONTAL TAIL

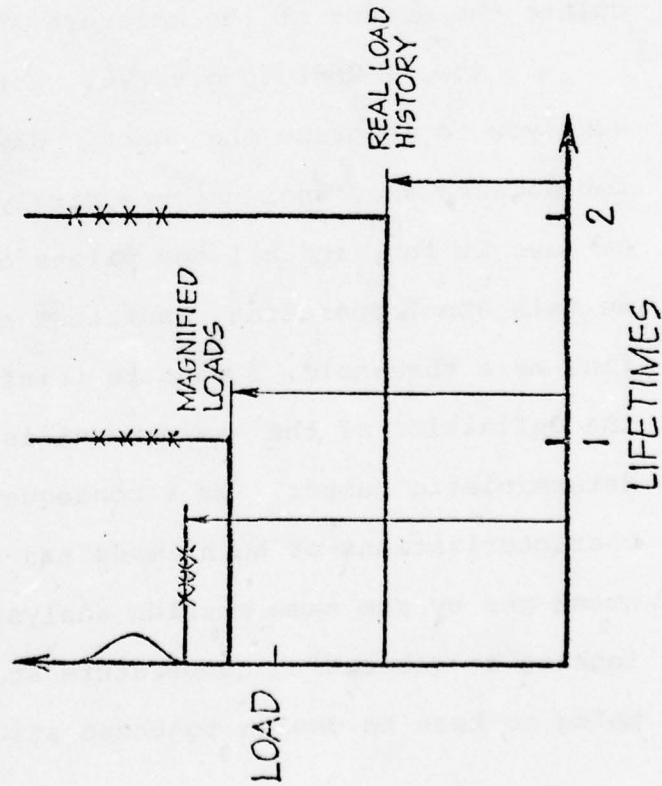


SHOWS HOT, WET, REAL TIME EFFECTS

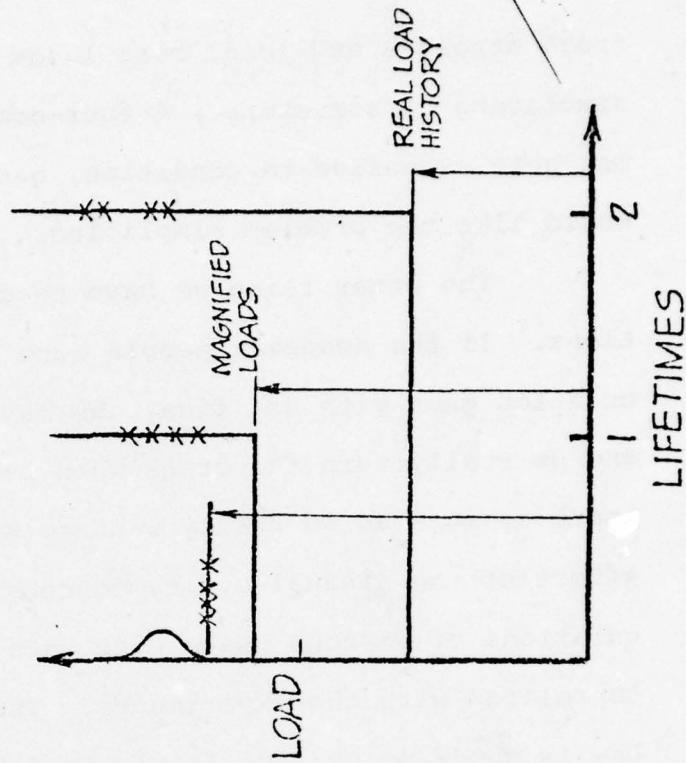
QUALIFICATION SUPPORT TEST PLAN

FLIGHT-BY-FLIGHT SPECTRUM

• RT, DRY, ACCELERATED



• HOT, WET, QUASI-REAL TIME

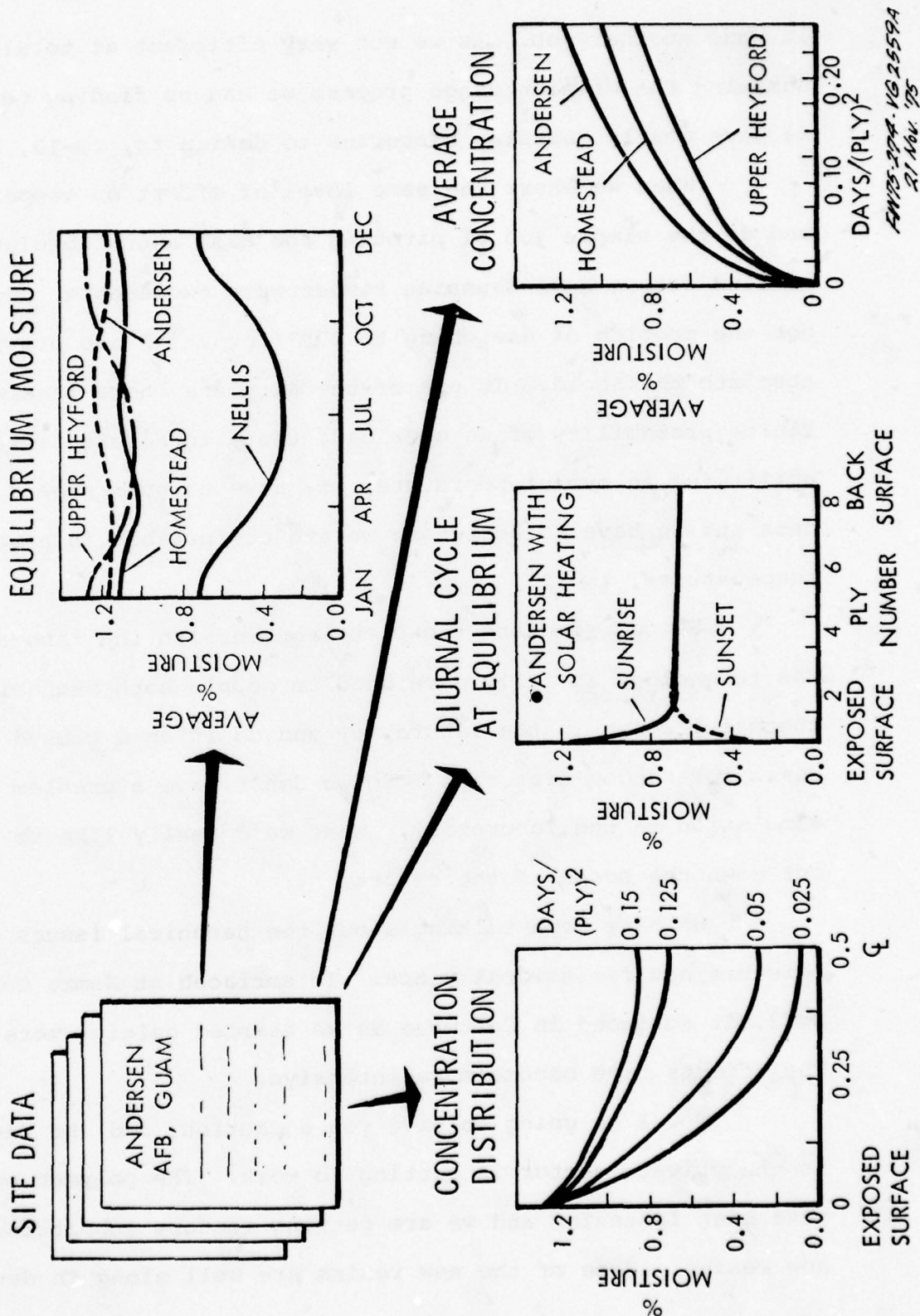


field stresses and local bolt loads and pretty large full scale simulators of structure. A four-component bonded joint specimen gets expensive to condition, gets expensive to test and we would like the problem simplified.

The other thing we have to do is to consider calculations. If the academic people here want to enter into the calculation game with us, fine. We have pretty intensive work hours and we really turn the crank when required. We have calibrated about as much as we really want to know about things like the effect of the diurnal cycle, concentration distributions and calculations of various usage site data. This data is fairly well correlated with the experiments. The correlation with Ficke's Law is good, so we feel fairly comfortable in being able to calculate the effect of the moisture state in the material, (W-9).

Now, I want to give you another surprise, and I don't want you to memorize the chart. When we talk about fatigue loads for an airplane, the customer rarely uses the airplane in the mode he buys it for, and all the pilots are different people, so when we talk about operating conditions and you want to run off and find me a threshold, I want to reinforce to you that the usage and the definition of the environment is a statistic. It's not a deterministic number. As a consequence we have to do statistical characterizations of both loads and now we have turned the same crank and by the same mission analysis we do on load, we are also looking at generating temperature statistical profiles. We are going to have to design to these structures considering statistics.

GROUND ENVIRONMENT EFFECTS HAVE BEEN CALCULATED



It adds another job. As we get very efficient at totally randomizing the mission usage process we end up finding out that we have nearly Gaussian histories to design to, (W-10, W-11).

When we exert the same level of effort on temperature and do the simple job of pivoting the data about absolute zero, we find out we have Gaussian temperature exceedence. So it's not the problem of designing to 270°F or 284°F and proving an absolute threshold. In use of the airplane there is always a finite probability of an overload, there is also a finite probability of an over-temperature. We have to guarantee a band of data and we have to design so we are comfortable in a range of temperatures, (W-12).

We can simulate these environments in the laboratory. The technology is fully developed to couple both mechanical and thermal loading in the laboratory and do it on a closed loop basis for random histories. So we don't have a problem with simulation in the laboratory. What we'd really like to do is cut down the scope of the effort.

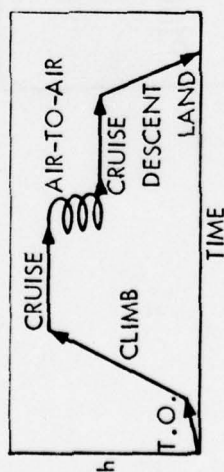
We have been talking about the technical issues of moisture now for several years. It surfaced at Nemma Colon in 1972, it surfaced in Columbus as we started gaining more data. The efforts have become more intensive.

Now I am going to give you a caution, and the caution is the private sector is getting to work. The polymer people have been listening and we are getting vendors submitting to us new resins. Some of the new resins are well along in development

THERMAL ENVIRONMENT AND LOADS ARE COMPATIBLE

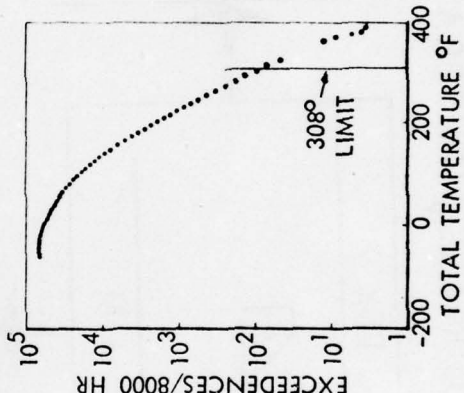
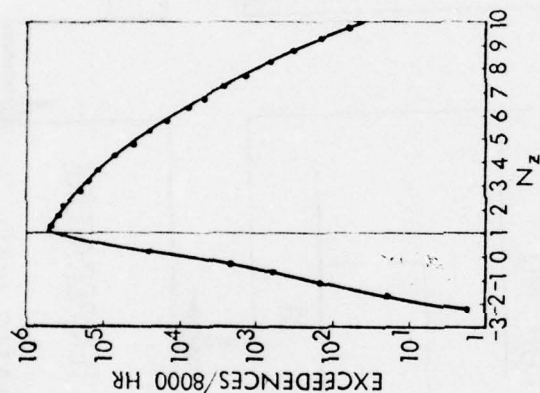
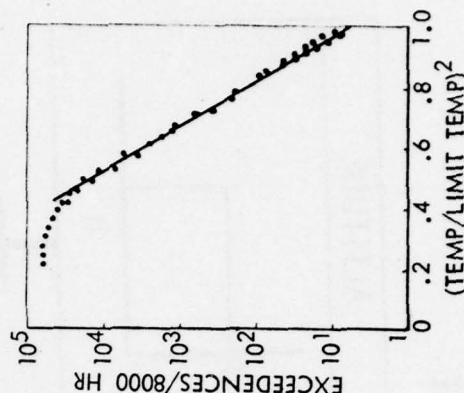
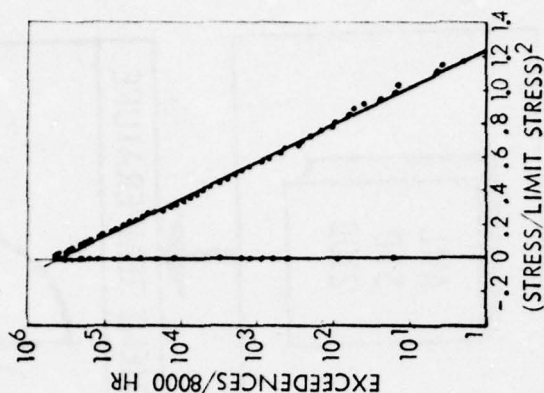
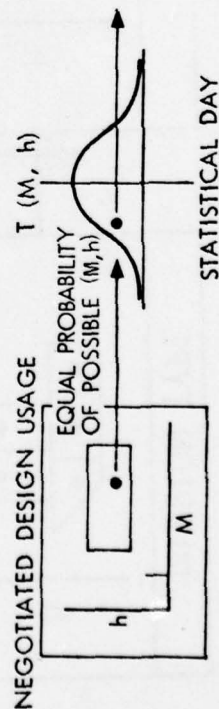
MISSION USAGE DEFINED

- 12 Mission Types
- Mission Segments
- 8000 Hours

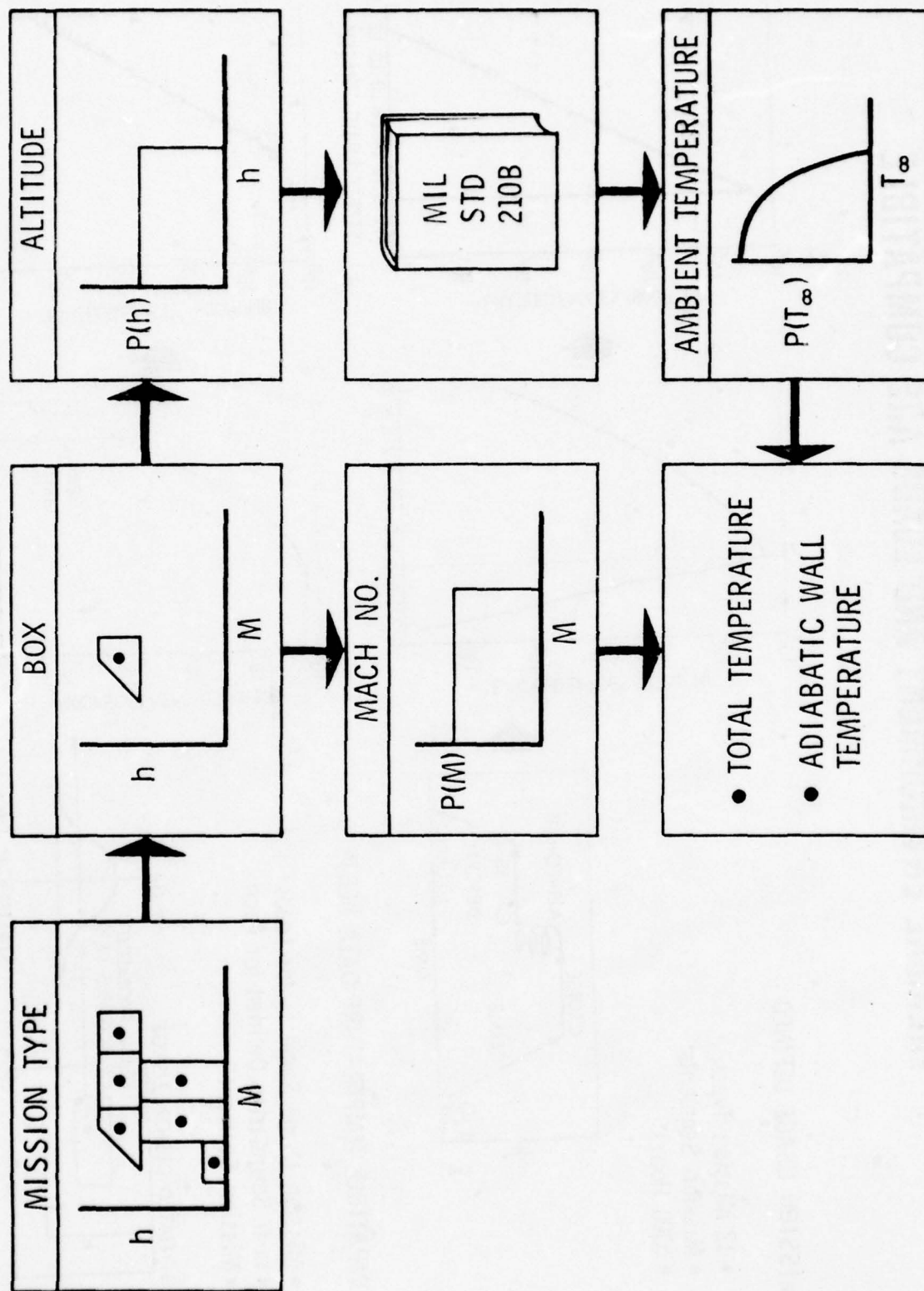


COMPATIBLE TEMPERATURE DATA DERIVED

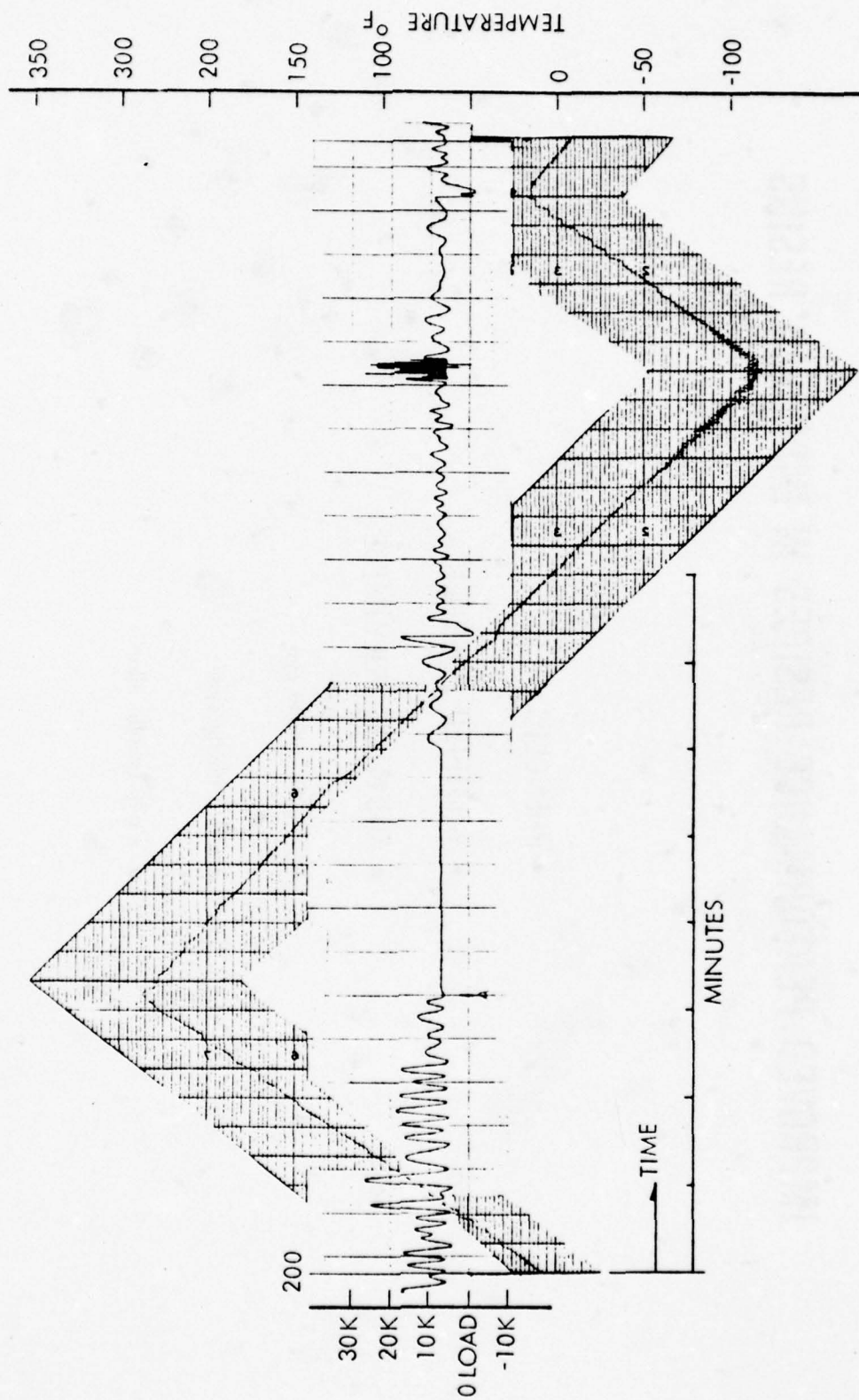
- Mission Usage Same as for Loads
- m-h Boundaries Defined for Each
- Mission Segment



RANDOM PROCEDURE \longleftrightarrow TEMPERATURE



PRECISE THERMO/MECHANICAL CONTROL IS REALIZED



IMPROVED PERFORMANCE RESIDES IN IMPROVED RESINS

- PHENOLIC
- MODIFIED PHENOLIC
- ADDITION POLYIMIDE
- It is the oldest type
- It is the oldest type
- It is the oldest type

W-13

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19 MAR '76

and they are making commercial prepregs from them. We are seeing these materials in our lab. One of these resins looks damn good. And I think there is going to be some more resins following that probably look a little bit better. We are real confident we can go into our F-16 production program in a matter of six months, transition to and get a more moisture resistant resin, and fully qualify it.

So my only message to you people is I think if you want to establish some technical reputation or make some money by getting a superior product on the market. I would suggest you hurry.

DR. PIPES: Thank you, Max.

I always have the same feeling after I listen to either Max or Dick Hadcock, there are no problems, that they are all solved.

So thank you, Max. I think that you did have some very astute observations and I think we do all recognize that you have in the neighborhood of twelve years of experience; certainly are one of the foremost authorities in this field and you were around when the first, what we have called, advanced composites were being developed and were very much instrumental in them. We thank you for your insight.

[Coffee Break].

DR. PIPES: It's my understanding that Mr. McBee did not make our meeting today and therefore we will go right on to the next scheduled speaker. In an effort to review the activities which have preceded these recent interests in moisture, we have invited Mr. Silvergleit of the David Taylor Naval Ship R & D Center to come and review with us the historical efforts in this area that the Navy has pursued. And to that end he will give us some information describing previous Navy efforts looking at moisture problems and fiber-reinforced materials.

C. Historical Reviews

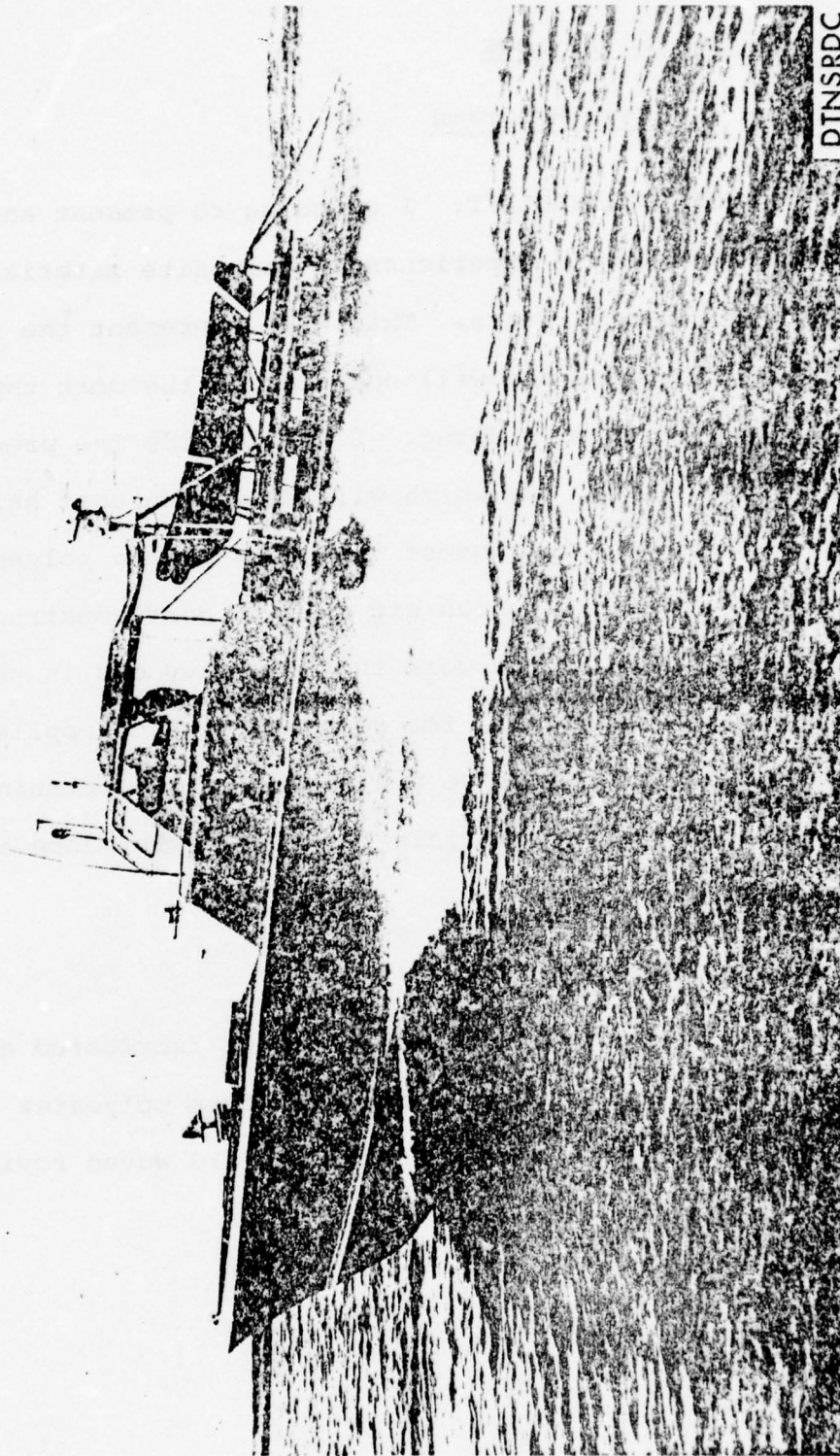
1. Navy Programs

MR. SILVERGLEIT: I am going to present an overview of the Navy's experience in composite materials over the last 25 to 30 years. This will represent the ship's side of the house and will not address the work that the Air people have been doing. I will divide the presentation into three areas, one which will deal with boat hull materials, which will address the glass fabric polyester and epoxy materials which are used in boat construction. The second area is the work that the Navy did in using S-glass epoxy materials for deep submergence applications, and, finally, the work we are now currently pursuing in advanced composite materials for high performance ship applications.

First slide (S-1) please.

Since about 1945, the Navy has fabricated about 3,000 boats which are normally fabricated from polyester resins reinforced with 24 ounce per square yard woven roving glass

52 FOOT GRP LANDING CRAFT,
SWIMMER RECONNAISSANCE (LCSR)



DTNSRDC

S-1

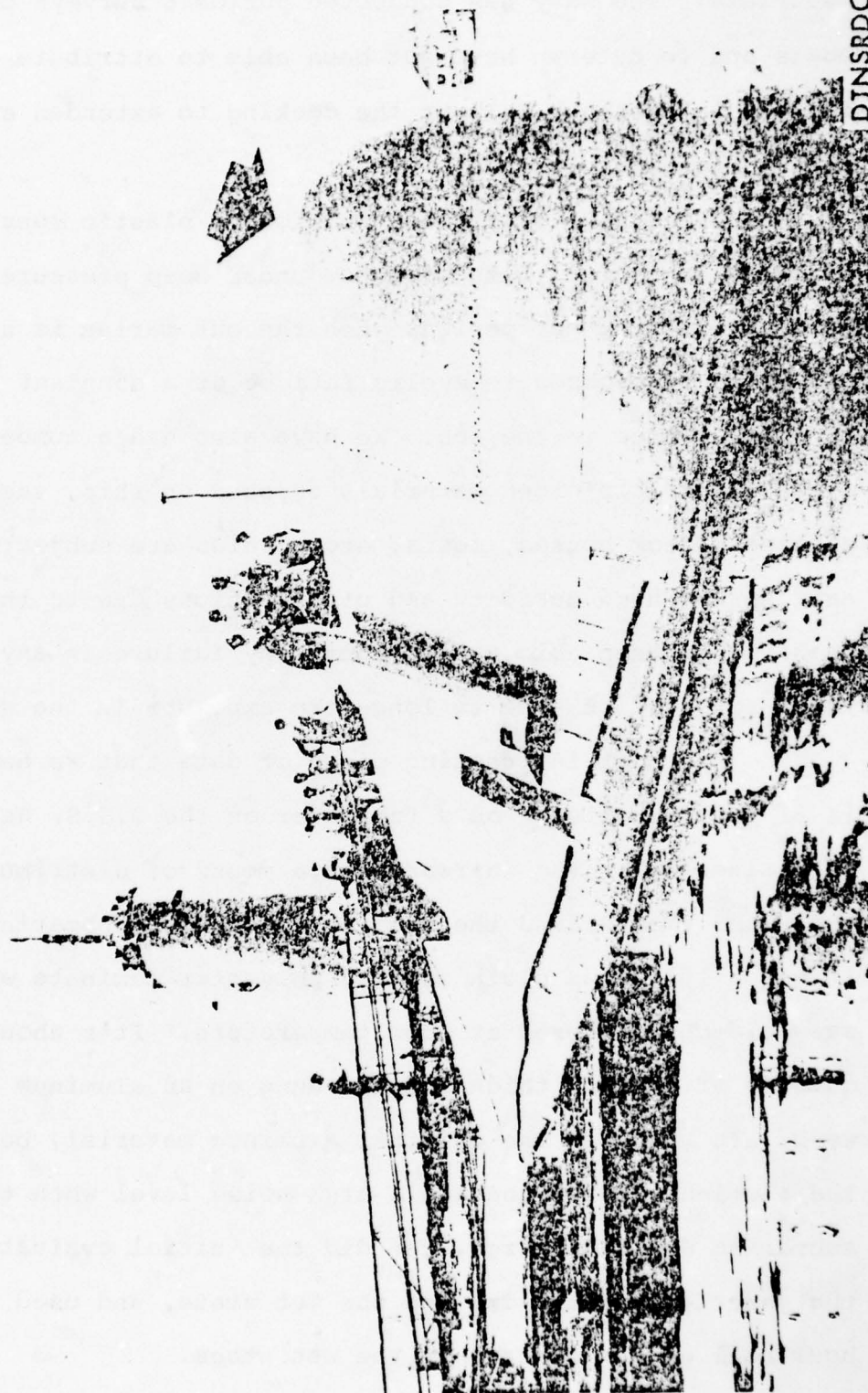
materials. The Navy has conducted periodic surveys of these boats and to date we have not been able to attribute any failure in the boat hull or the decking to extended exposure to the marine environment.

This (S-2) is a glass reinforced plastic sonar dome which is subjected to submergence under deep pressure, has prolonged drying out periods when the out marine is surfaced and which is exposed to cyclic fatigue or a constant load due to the exposure in the sea. We have also had a number of other fiber reinforced materials exposed on ship, such as, antennas, deck houses, masts, etc., which are subjected to salt spray, high humidity and other actions due to the sea. We have not been able to attribute any failure in any of these applications due to long-term exposure in the sea.

The most interesting piece of data that we have is 11 year experience on a fairwater on the U.S.S. Halfbeak submarine. (S-3) The fairwater is a means of distributing the water flow around the conning tower of a submarine. It was a 181 glass cloth fabric, polyester laminate which was laid-up and cured at room temperature. It's about a quarter of an inch thick and was hung on an aluminum framework. It replaced the original aluminum material, because the aluminum dished and had a high noise level when the submarine would submerge. We did the initial evaluation of the material in the dry and the wet state, and used the two-hour boil as our control in the wet stage.

The interesting data is that 11 years later after

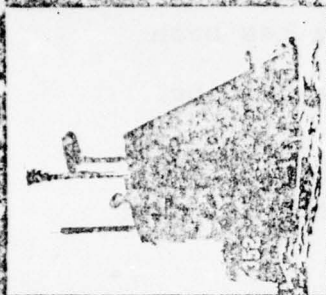
PLASTIC SONAR DOME



DTNSRDC

GLASS REINFORCED PLASTIC FAIRWEATER

EFFECT OF 11 YEARS SERVICE ON USS HALFBEAM



PROPERTY	CONDITION	ORIGINAL DATA	CURRENT DATA (11 YRS. SERV.)	SPECIFICATION ^(a) REQUIREMENT
FLEXURAL STRENGTH, PSI	DRY	52,400	51,900	50,000
	WET ^(b)	54,300	46,900	45,000
FLEXURAL MODULUS, PSI x 10 ⁻⁶	DRY	2.54	2.52	2.50
	WET	2.49	2.37	2.30
COMPRESSIVE STRENGTH, PSI	DRY	-	39,100	33,000
	WET	-	35,600	28,000

(a) MIL-P-17549
(b) TWO HOUR BOIL

DTNSRDC

S-3

actual service there is no sign of any deterioration in the panels. There was some elongation of the boat hulls and this was due to the inexperience of the shipyard in the installation of these materials. But as you can see, there has been essentially no loss in the strength and the modulus remains relatively unaffected. And what is most important is that after this extended exposure we are still meeting the original specification requirements.

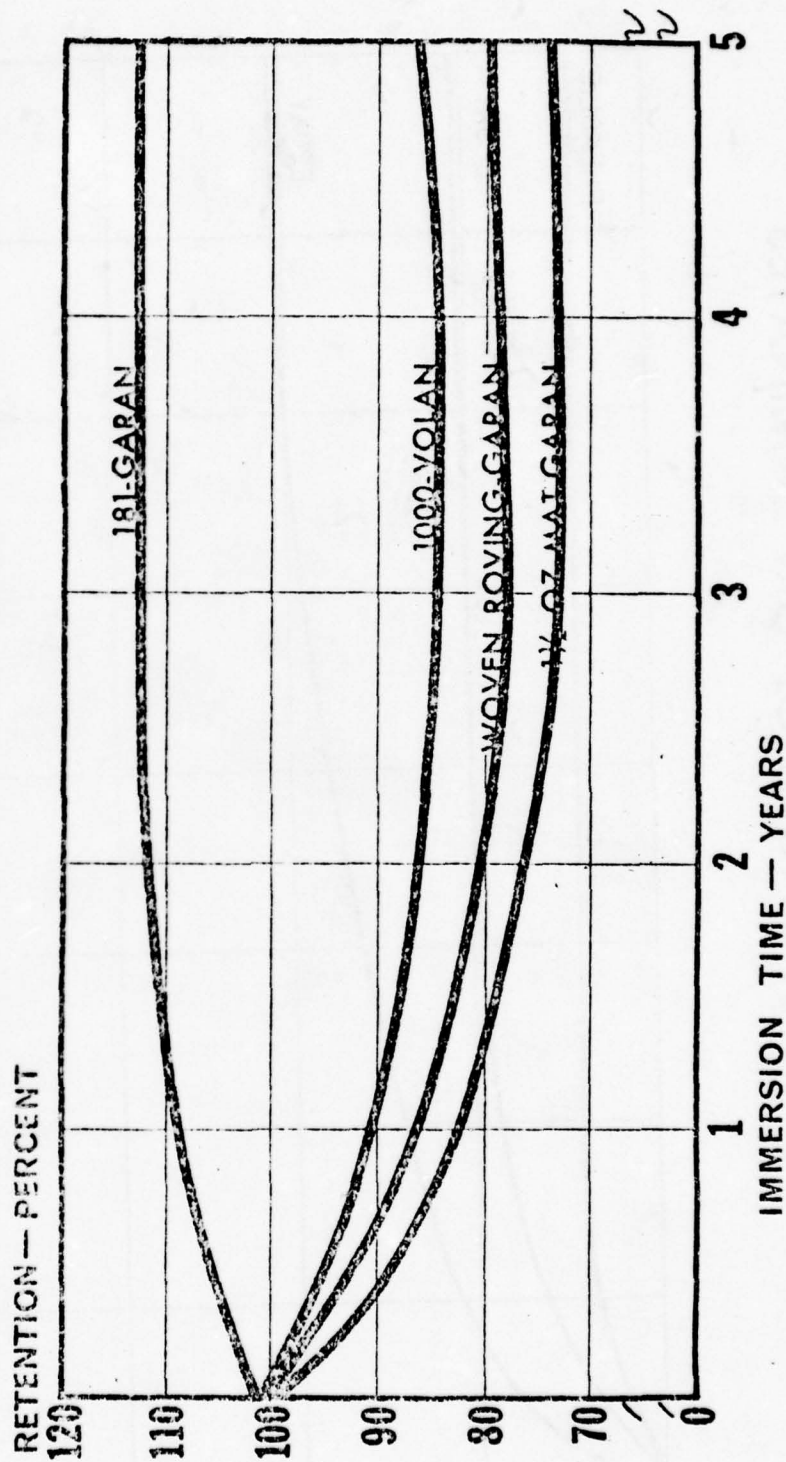
About 25 years ago when the Navy initiated its program on glass reinforced plastics for small boat application, it was decided to subject representative materials to long term exposure in the sea.

Laminates were made by the wet lay-up, room temperature cure system, and exposed in the sea at Kurie Beach. They were removed every year for five years. We observed (S-4) that degradation occurs in a relatively short time and then the curve flattens out throughout the immersion period with no other degradation. The interesting thing was that degradation, when it happens, happens in a relatively short time.

We were also interested in other types of resins, and this slide (S-5) shows a phenolic and two epoxy materials which were subjected to an extended boil for 16 hours. Again we noticed that degradation occurs within a short time frame. This is, I believe, characteristic of all of the materials that we have been investigating when they are exposed to water at room temperature or after extended boil.

You will see the same results on the materials used

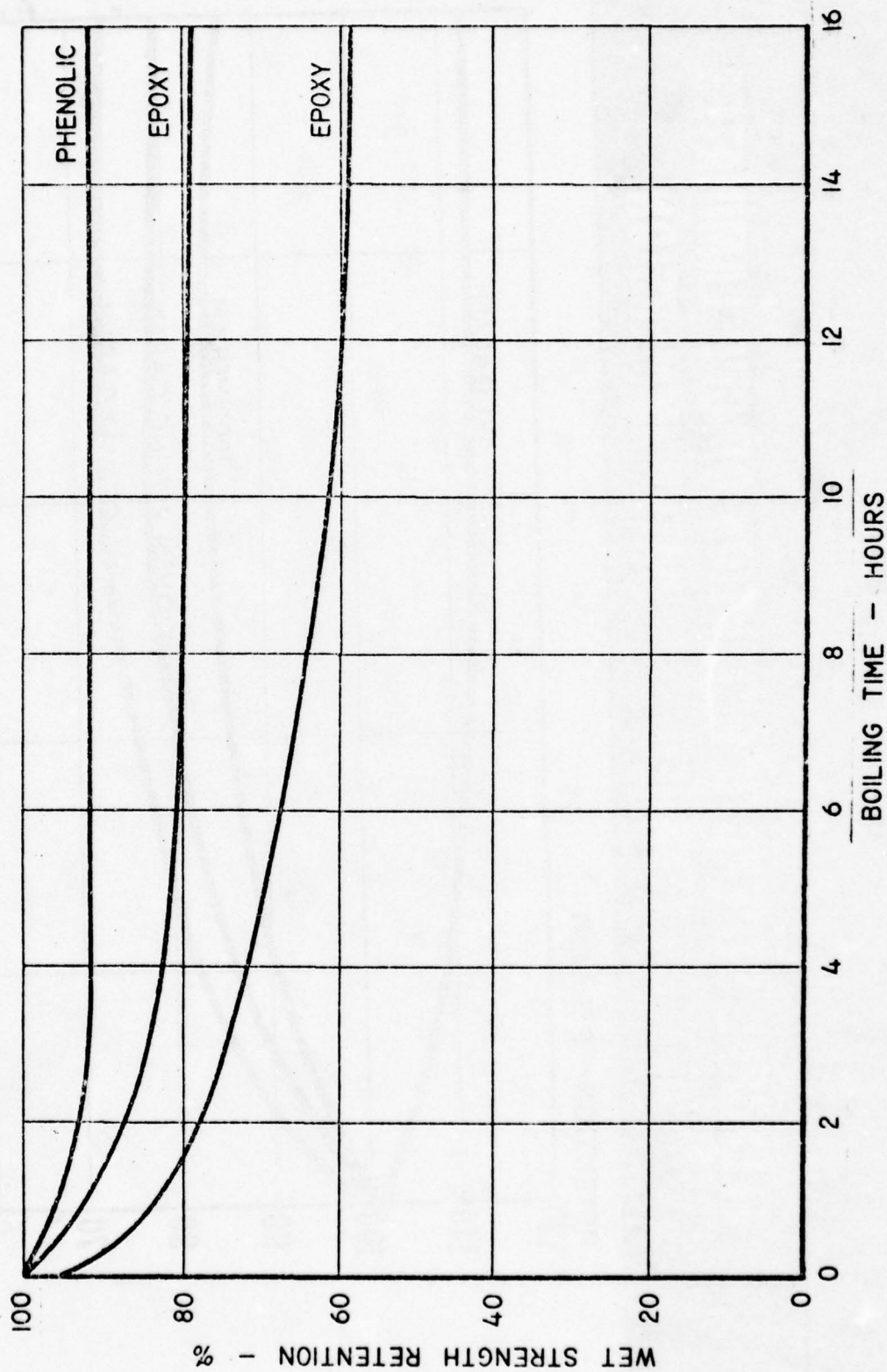
FLEXURAL STRENGTH RETENTION OF GRP LAMINATES AFTER EXTENDED SEA WATER IMMERSION



S-4

DTNSRDC

EFFECT OF IMMERSION IN BOILING WATER ON FLEXURAL STRENGTH OF GRP LAMINATES



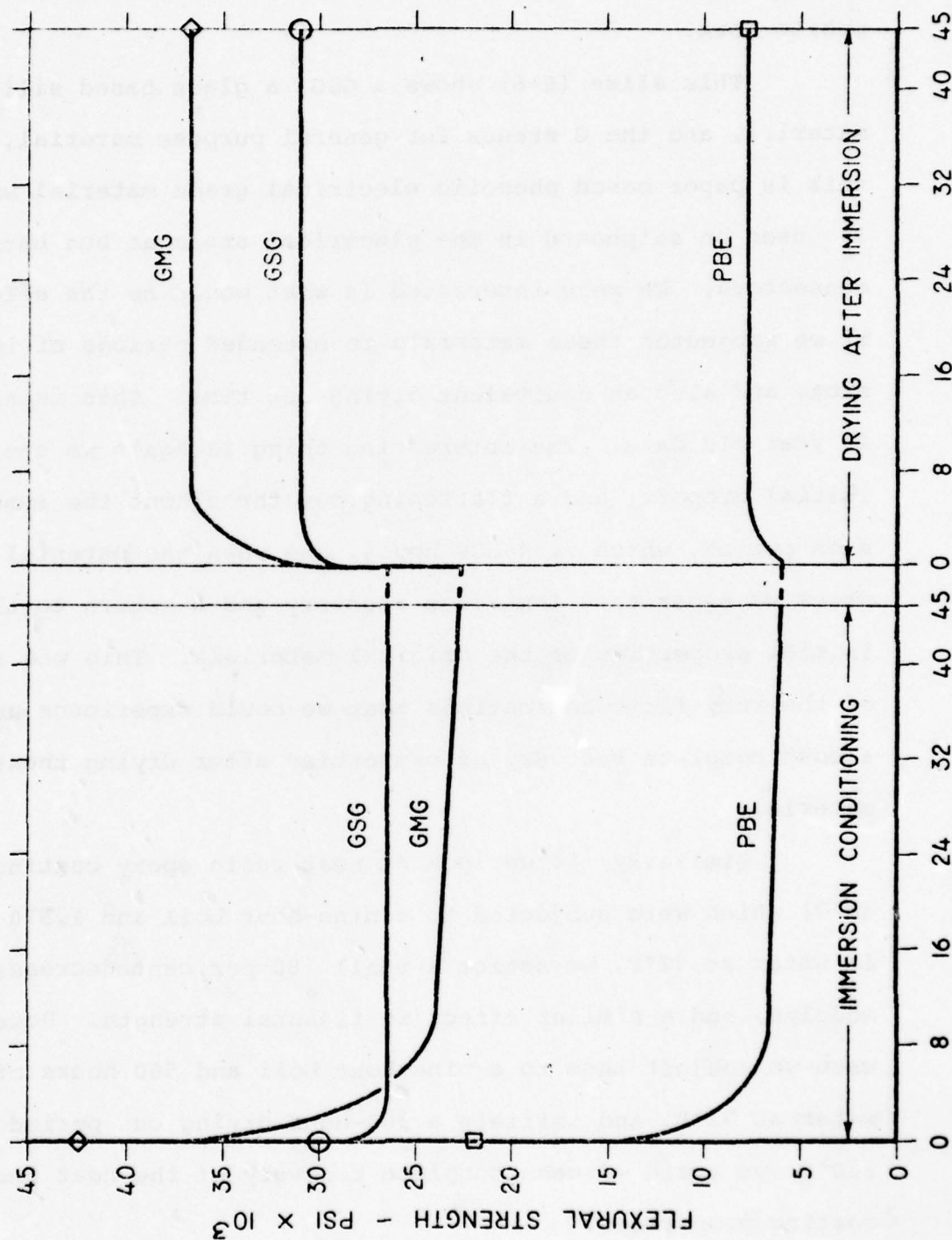
on the deep submergence program and also on the advanced composite work.

This slide (S-6) shows a GSG, a glass based silicone material, and the G stands for general purpose material, and this is paper based phenolic electrical grade material which is used on shipboard in the electrical areas as bus bars and connectors. We were interested in what would be the effect if we subjected these materials to extended periods of immersion, and also an equivalent drying out time. This is about 25 year old data. The interesting thing is again we see the initial dropoff, and a flattening out throughout the immersion period, which is 4,500 hours, and when the material dries we experience immediate recovery and a return to the initial properties of the original materials. This was some of the very first indications that we could experience an almost complete recovery of properties after drying these materials.

Similarly, if we look at neat resin epoxy castings, (S-7) which were subjected to a nine-hour boil and 1,570 hours in water at 72°F, we notice a small 80 per cent decrease in modulus, and a similar effect in flexural strength. However, when we subject them to a nine-hour boil and 560 hours of water at 72°F, and initiate a 900-hour drying out period at 140°F, we again witness complete recovery of the neat resin casting properties.

I have discussed some of the work we did with total immersion and boil for these materials. In small boat

EFFECT OF WATER IMMERSION AND SUBSEQUENT DRYING ON PLASTIC LAMINATES



TIME - HOURS $\times 10^2$

S-6

DTNSRDC

EFFECT OF WATER IMMERSION AND OF SUBSEQUENT DRYING ON EPOXY CASTINGS

CONDITION	MODULUS (PSI $\times 10^5$)	FLEXURAL STRENGTH (PSI $\times 10^3$)
<p>DRY</p> <p>9 HR BOIL —1570 HR IN WATER AT 72 °F</p> <p>9 HR BOIL—560 HR IN WATER AT 72 °F + 900 HR DRY IN AIR AT 140 °F</p>	<p>5.04</p> <p>4.87</p> <p>5.43</p>	<p>19.1</p> <p>15.6</p> <p>19.2</p>

DTNSRDC

S-7

construction we require the fabricator to store the glass and the resin in a temperature and humidity controlled atmosphere. To verify the need for these controls we initiated a program to see what the effect would be on the neat resin, on the glass, and on the composite if we could induce water into the resin or into the glass.

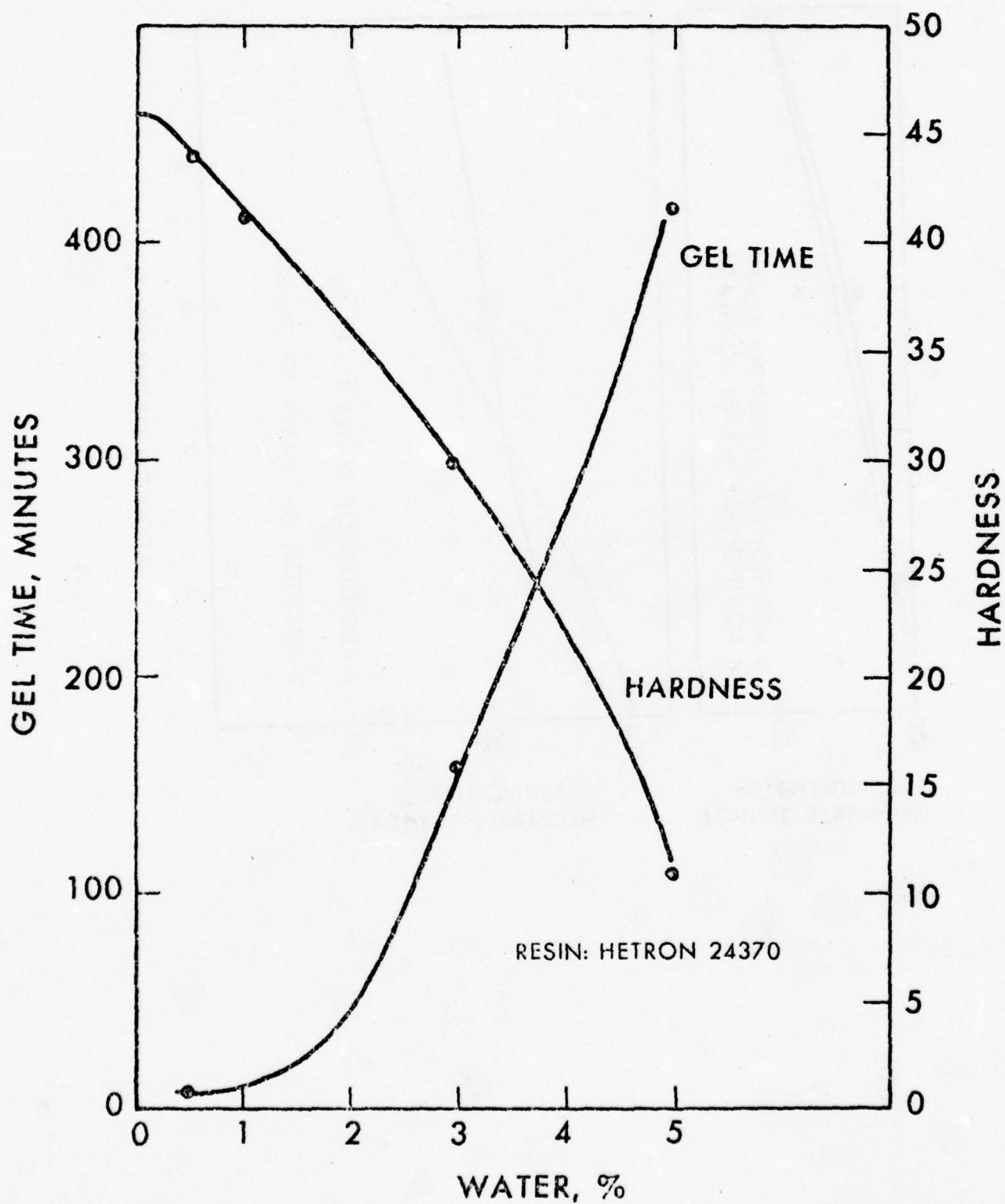
When water was added to the resin phase of Hetron 24370, which is the conventional fire-retardant boat material, we decreased the hardness and increased the gel time. (S-8)

This slide (S-9) shows the strength retention of these materials with the addition of water. When water was added to the glass it resulted in a sharp decrease in flexural strength, and not as significant a decrease in the tensile strength. It affects both the warp and the fill, as one would expect.

One of the ways that the Navy determines the quality of boat laminates, which are normally made in shipyards, is by inspection, visual inspection of the laminate itself. The resin system has to be clear so that the inspector can get a look at it. The Navy has a requirement that the laminate have a certain amount of light transmission. When water was added to the resin and glass phase of a laminate we experienced a significant decrease in the translucency of these materials. (S-10)

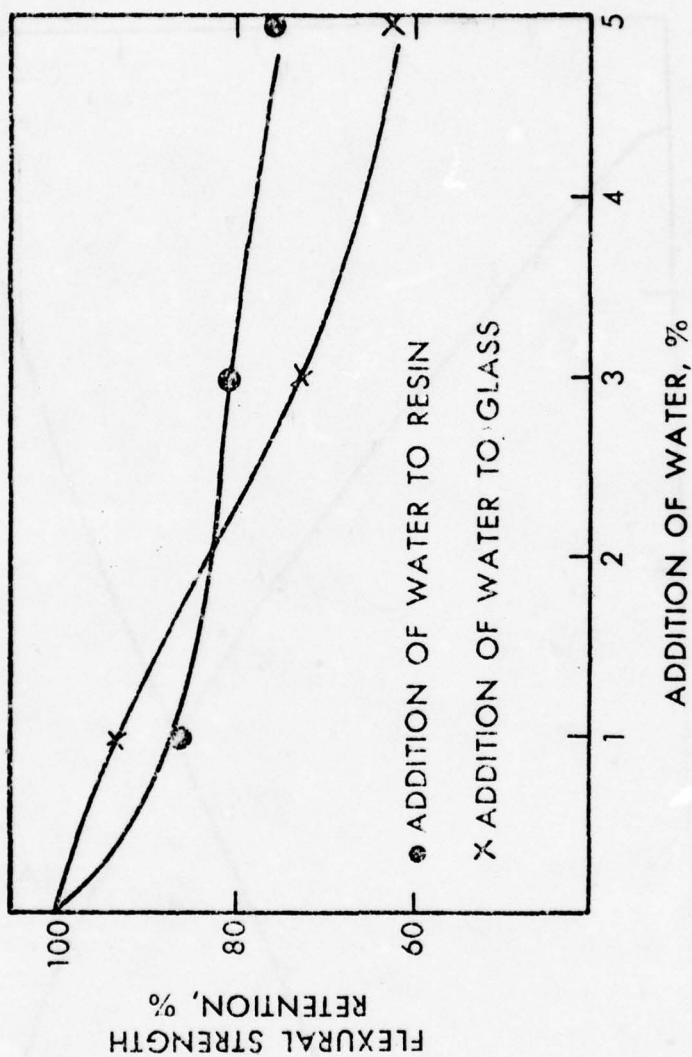
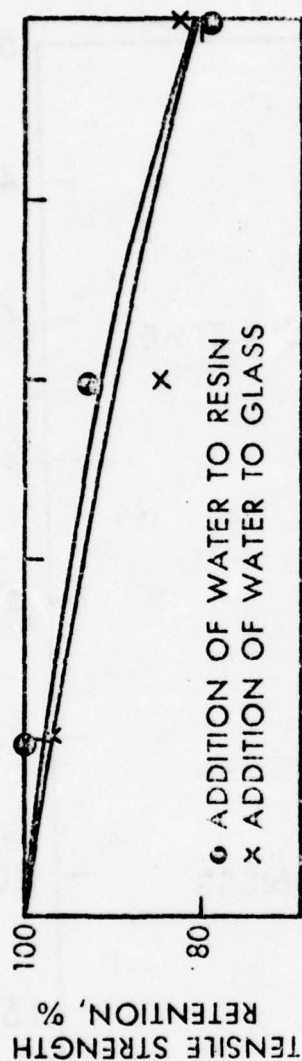
This slide (S-11) shows "white laminate" and you can see the white streaks throughout the glass. This is in a

EFFECT OF STORAGE MOISTURE ON NEAT RESIN CASTING PROPERTIES

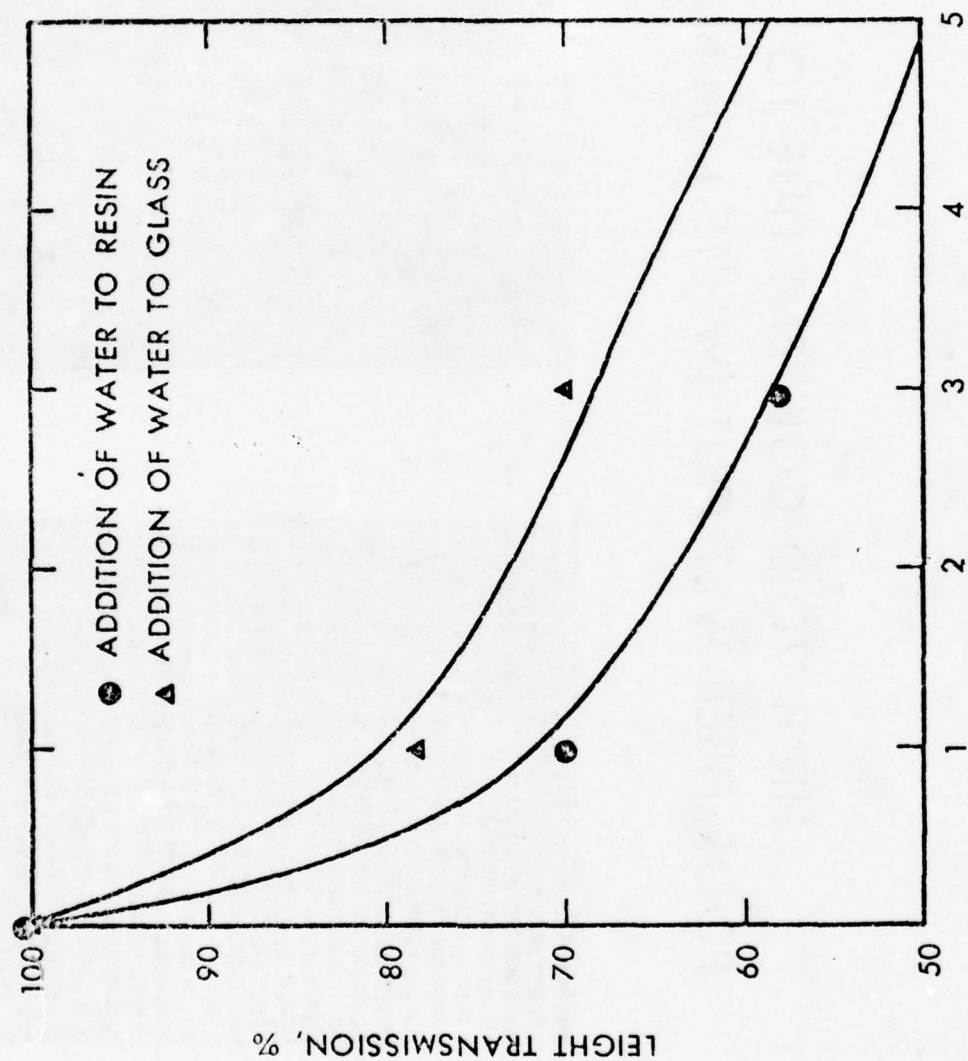


DTNSRDC

EFFECT OF STORAGE MOISTURE ON LAMINATE STRENGTH



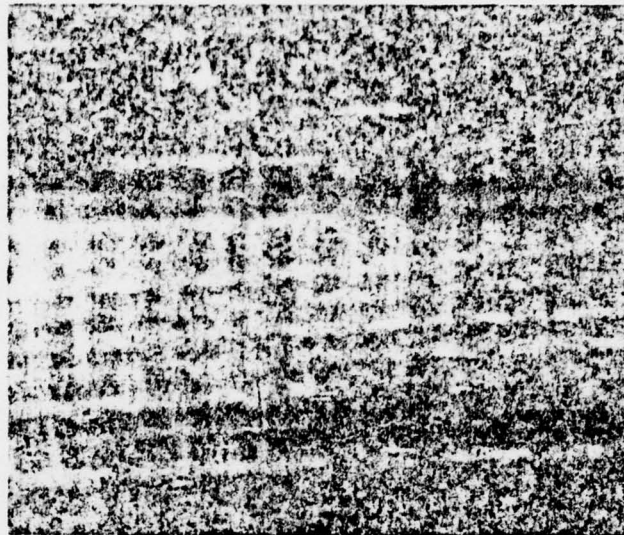
EFFECT OF STORAGE MOISTURE ON LAMINATE TRANSLUCENCY



S-10

DTNSRDC

HIGH VOID CONTENT DUE TO
POOR FIBER WET OUT (WHITE LAMINATE)



S-11

DTNSRDC

24 ounce per square yard woven roving polyester laminate, made in a boatyard. An analysis was made of the glass fabric and it was found that a change was made by the manufacturer in the binder content of the woven roving. The increase in the binder content reduced the wet-out characteristics of the polyester resin and prevented the ingress of resin between the filaments, and resulted in what was called "white laminate". These, in fact, became high void areas which had poor wet strength retention.

Work was also done (S-12) on the effect of the finish on the interface between the glass and the resin system. This is a 181 glass with a Silane finish, a 112 type glass which has been heat cleaned and a Silane finish. The decrease in strength retention is significant especially in the material without the finish. The same results apply to the polyester, (S-13) as well as the epoxies. The effect of the finish is quite significant on these materials. There was a significant amount of work done on the effect of the interface between the resin and the glass, particularly in the development of improved finishes to improve the wet strength of polyester laminates.

A decision was made by the Navy to enter into a program on utilizing composite materials for deep submergence applications. An analysis was made at that time, which was prior to the development of the current high yield strength steels and the development of new welding techniques for titanium, which showed that S-glass epoxy materials were the only materials

EFFECTS OF CHEMICAL COUPLING AGENTS ON WATER RESISTANCE OF REINFORCED PLASTIC LAMINATES

REINFORCEMENT AND FINISH	POLYESTER LAMINATES				EPOXY LAMINATES			
	FLEXURAL STRENGTH, 1000 PSI				FLEXURAL STRENGTH, 1000 PSI			
	ORIG- INAL	BOIL- ING WATER, 7 DAYS	ROOM TEMP. WATER		ORIG- INAL	BOIL- ING WATER, 7 DAYS	ROOM TEMP. WATER	
			6 DAYS	30 DAYS			6 DAYS	30 DAYS
STYLE 181 GLASS CLOTH WITH SILANE FINISH	76.3	66.1	80.7	79.0	78.4	54.0	74.9	71.4
STYLE 112 GLASS CLOTH, HEAT CLEANED WITH SILANE FINISH	71.1	54.4	64.5	62.4	79.6	41.0	78.3	74.0
(SAME AS ABOVE, BUT WITHOUT SILANE FINISH)	49.6	18.2	20.5	19.0	79.7	19.8	72.8	65.9

S-12

DTNSRDC

EFFECTS OF DEEP OCEAN EXPOSURE ON GLASS-REINFORCED PLASTIC LAMINATES

	EPOXY LAMINATE			POLYESTER LAMINATE		
	INITIAL	AFTER EXPOSURE IN THE OCEAN AT 5700 FT		INITIAL	AFTER EXPOSURE IN THE OCEAN AT 5700 FT	
		111 DAYS	1045 DAYS		111 DAYS	1045 DAYS
COMPRESSIVE STRENGTH, PSI	136,800	115,600	71,600	33,000	31,100	33,500
COMPRESSIVE MODULUS, PSI	5.97×10^6	5.84×10^6	6.13×10^6	2.72×10^6	2.61×10^6	2.90×10^6
FLEXURAL STRENGTH, PSI	—	—	—	38,800	39,500	38,100
FLEXURAL MODULUS, PSI	—	—	—	2.60×10^6	2.59×10^6	2.50×10^6
INTERLAMINAR SHEAR STRENGTH, PSI	5900	4000	1760	1810	1680	1880

DTNSRDC

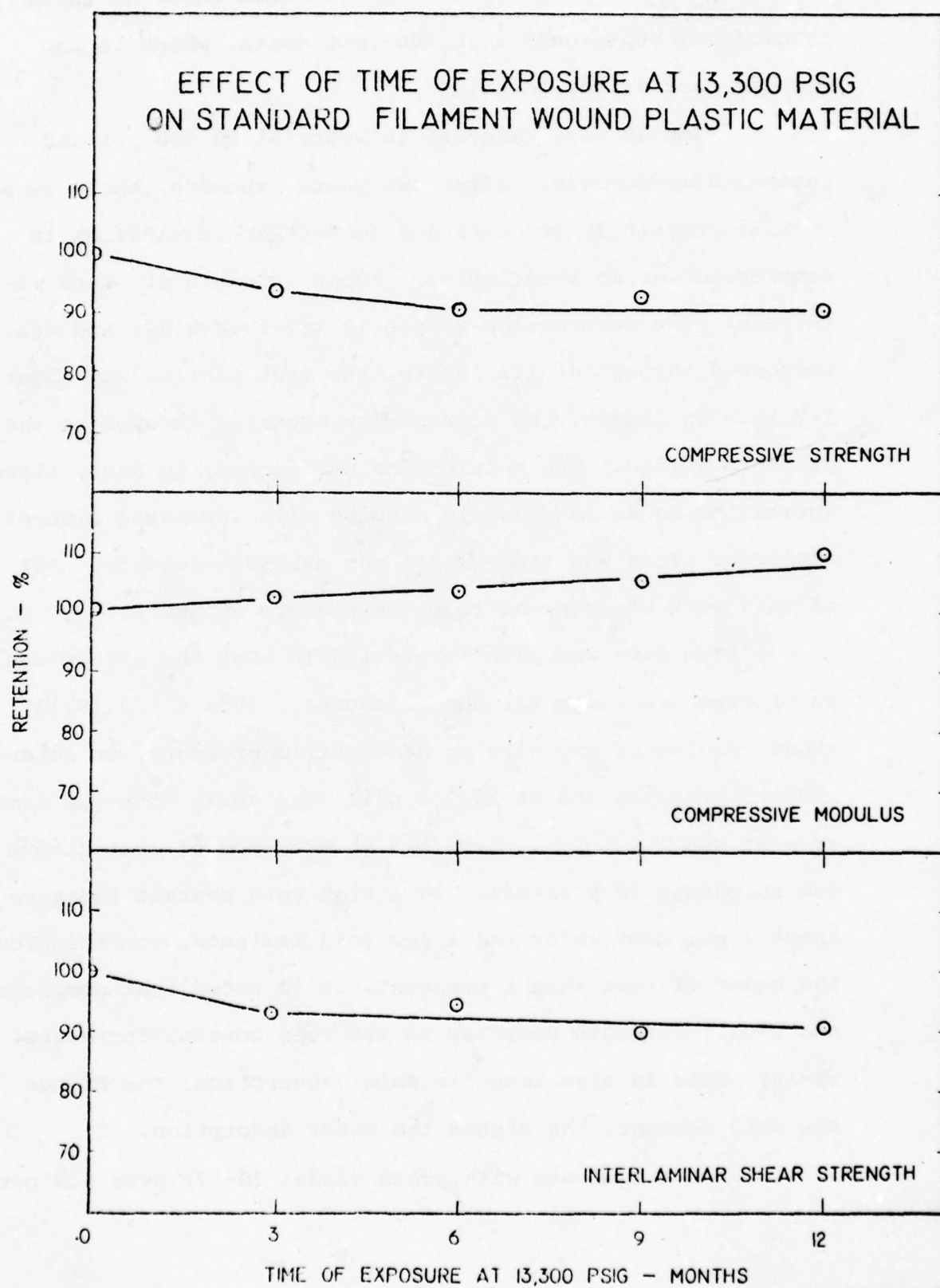
S-13

that could get a weight-to-displacement ratio of about a half at a 30,000 foot submergence level, which is the deepest part of the ocean. A program was initiated between the Navy laboratories and the contractors to develop these materials for deep submergence applications.

In early work materials were submerged at a 5,700 foot depth. These are the results after 111 days for an epoxy laminate and a polyester laminate. The polyester laminate was fabricated in the laboratory and which the composition was known. The epoxy laminate was supplied by a fabricator. There was no identification of the glass, or of the finish. After 111 days of exposure there was a slight drop-off in the strength, while the polyester was relatively unaffected.

After 1,045 days exposure it was observed that the epoxy laminate retained about half its strength while the polyester was unaffected. These results were atypical for epoxy materials. The cause for this unusual result was that the manufacturer supplied the wrong material. The sizing that was on the glass was of the wrong composition, and was not meant for water immersion.

This (S-14) is the data that was generated in the laboratory on the exposure of filament wound materials. These are S-glass epoxy materials, with the glass being the S-901 material. Laminates were wound in a two-to-one orientation with two plies, going in the zero degree direction, and one ply oriented in the 90° direction. It was wound in a bidirectional mold which produced two 1/4-inch flat plates.



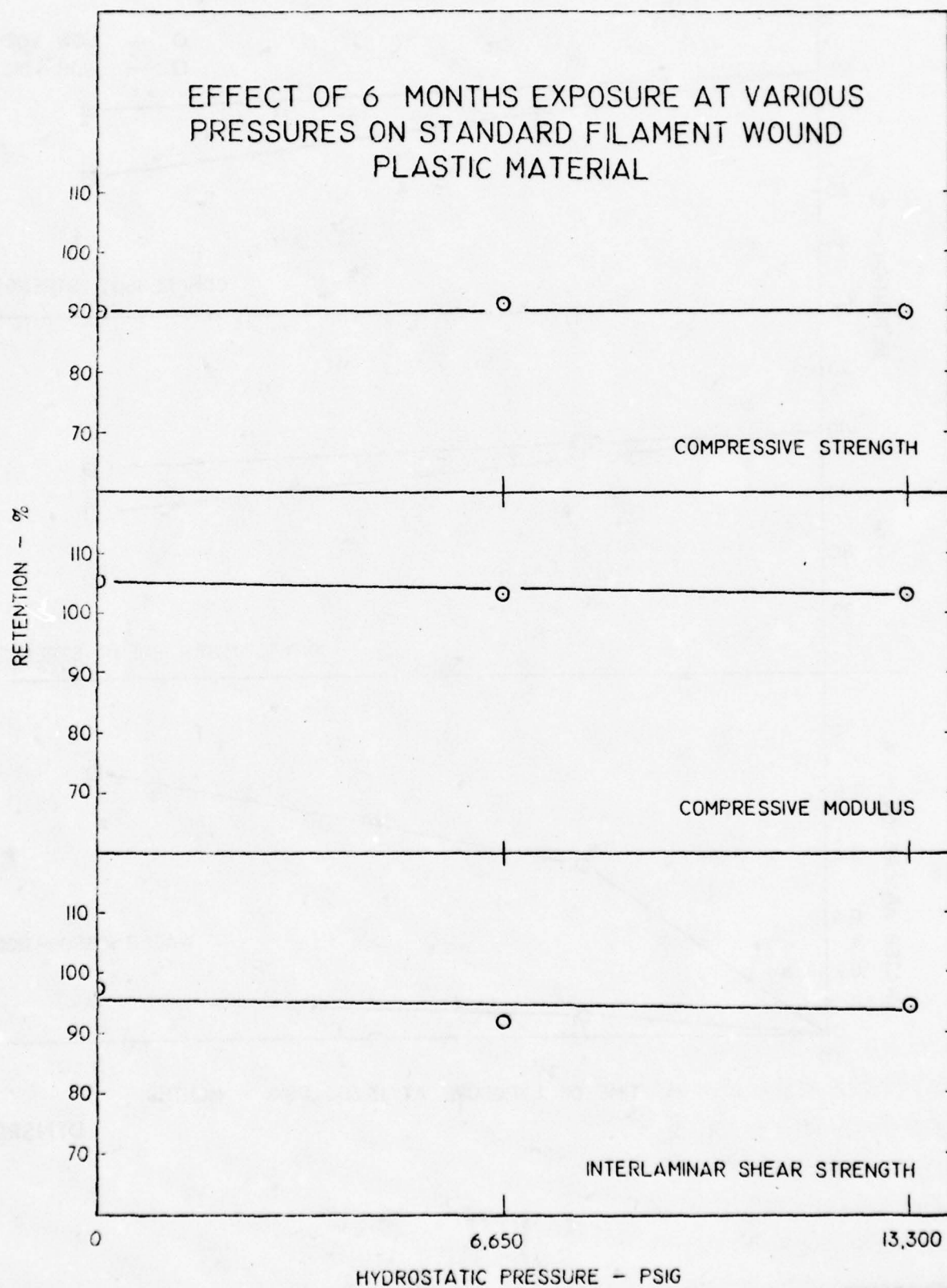
S-14

All samples were cut from the plates and samples were immersed with all edges exposed to water. Thirteen thousand three hundred psi represents a 30,000 foot depth, which is the deepest part of the ocean.

Samples were immersed in water at 13,300 psi and periodically removed. After two years exposure, there is an initial dropoff in strength and no further degradation in compression or in interlaminar shear strength of these materials. The compression sample is 1/2 inch wide, and was supported throughout its length, the test section was about 1/2 inch in length. No degradation occurred throughout the exposure period. The modulus was unaffected, in fact, there appears to be an increase in modulus with increased time of exposure. This was true of all our exposure results. All of this work was done at room temperature exposure.

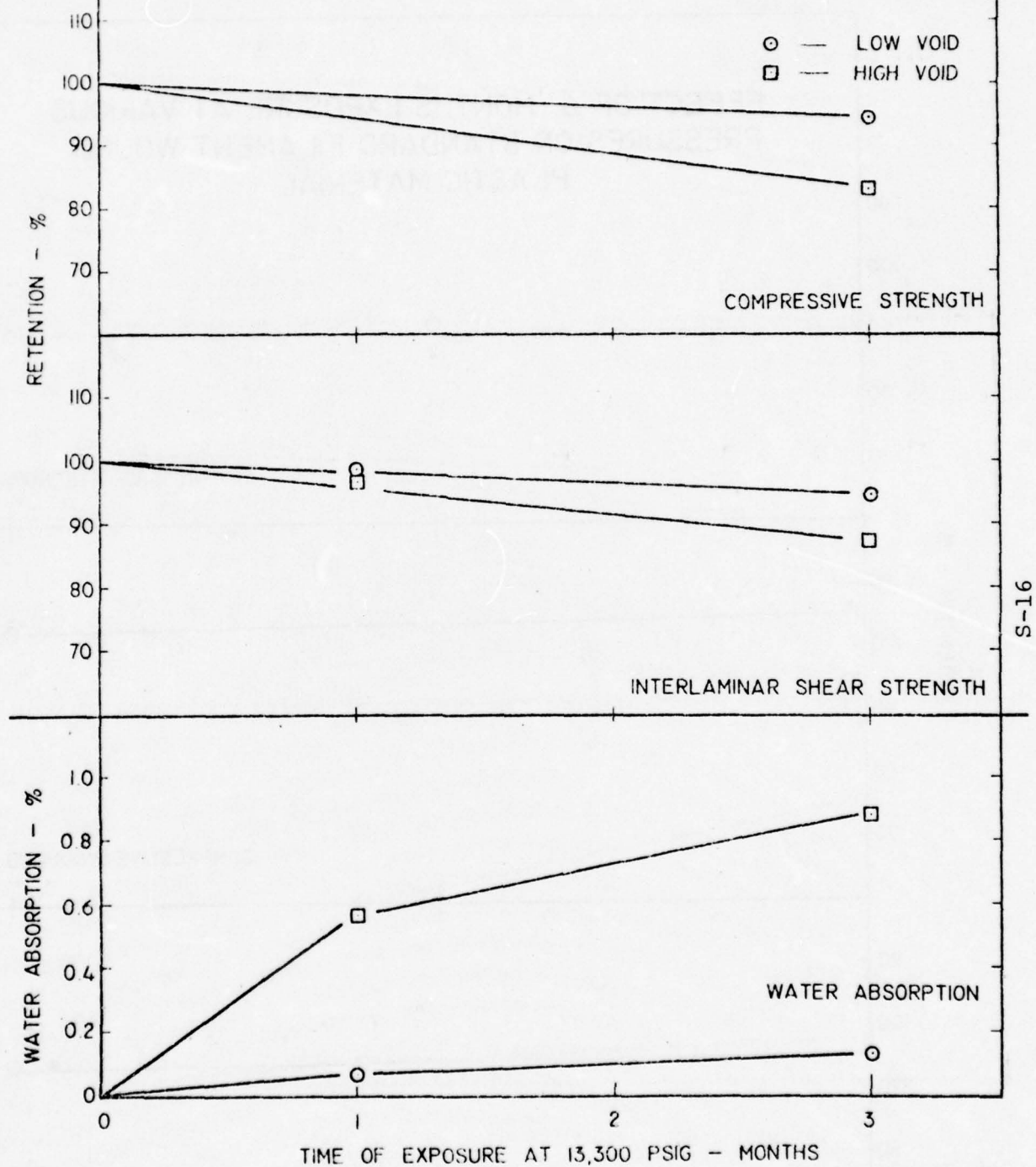
The Navy was also interested in what the effect would be of exposure under various pressures. This slide (S-15) shows results of exposure at atmospheric pressure, an intermediate pressure and at 13,300 psi. And again with the same type of small samples, there was no evidence of degradation due to change in pressure. In a high void content laminate of about 2 per cent voids and a low void laminate, something on the order of less than 1 per cent, it is noted that compression and shear strength decrease as the void content increases. (S-16) This is also true for water absorption, the higher the void content, the higher the water absorption.

For a laminate with gross voids, (S-17) over 6.2 per cent



S-15

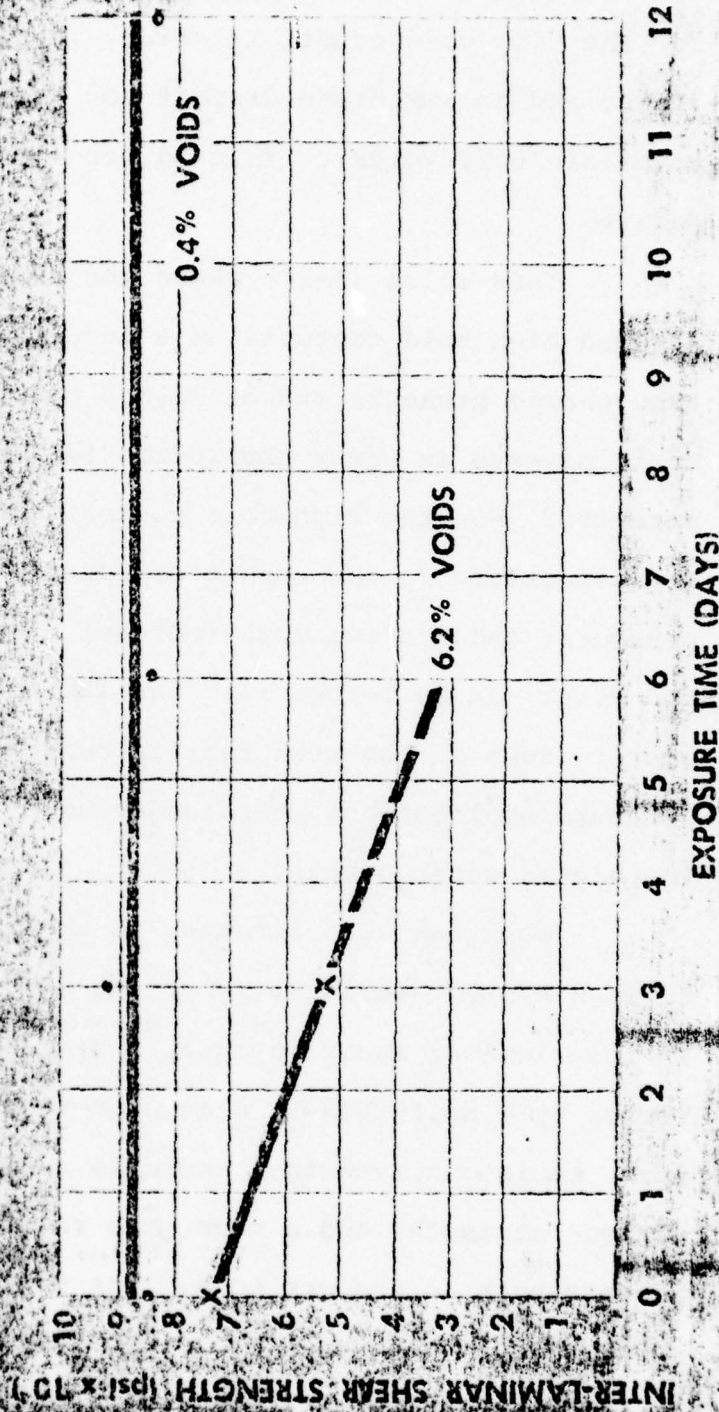
EFFECT OF TIME OF EXPOSURE AT 13,300 PSIG ON¹⁴⁴
SPECIALLY FABRICATED LOW AND HIGH VOID
FILAMENT WOUND PLASTIC MATERIAL



S-16

DTNSRDC

INFLUENCE OF VOID CONTENT ON FILAMENT WOUND GLASS REINFORCED EPOXY LAMINATES



AT 20,000 psi HYDROSTATIC PRESSURE

S-17

DINSRDC

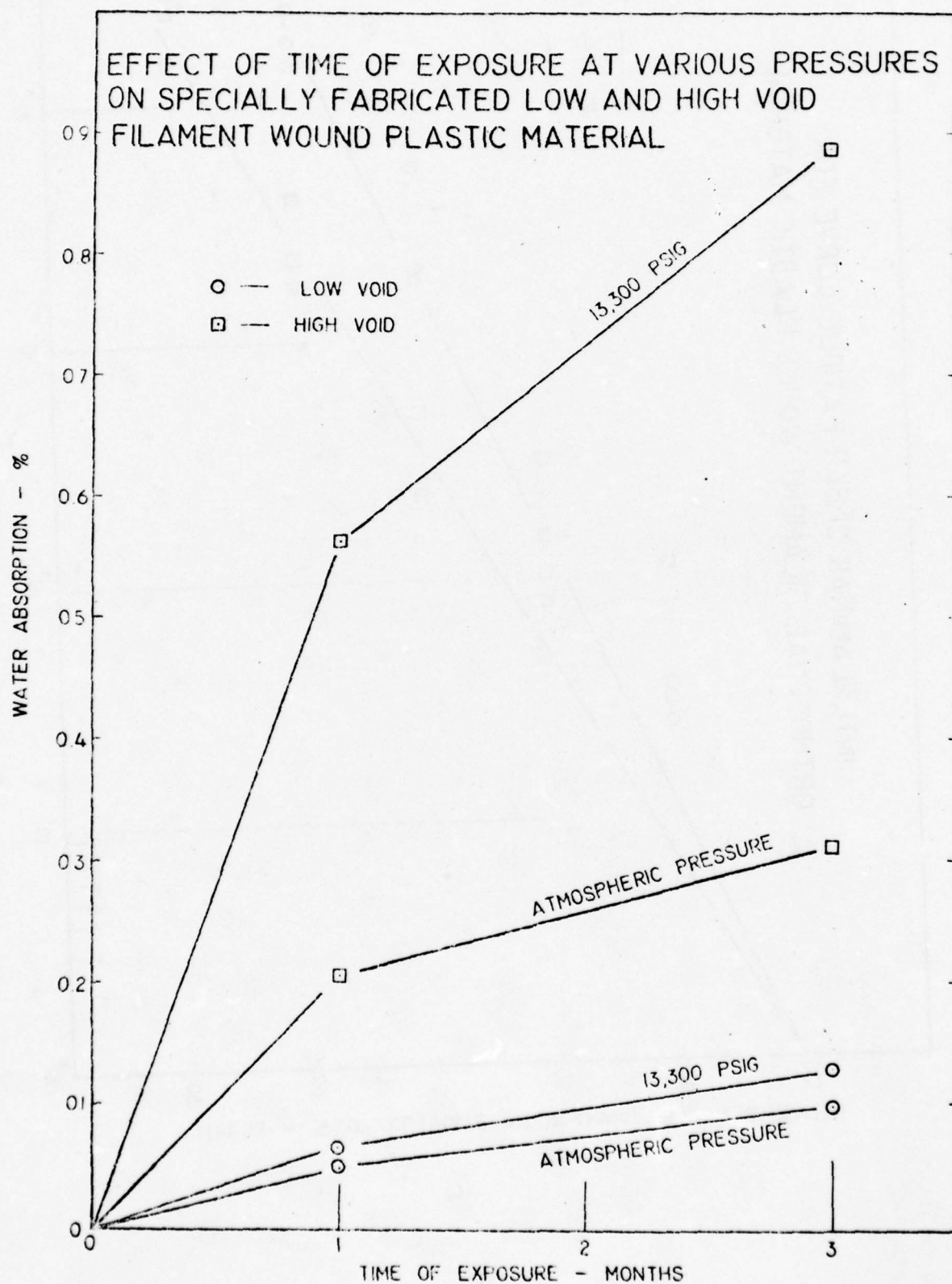
COPY AVAILABLE TO DDC DOES NOT
PERMIT FULLY LEGIBLE PRODUCTION

voids for the same material, there is no decrease in strength for the "low void count" material, less than half a per cent voids, and an immediate dropoff for the very high void content material (6.2% voids). This is for a 30,000 foot depth exposure.

This slide (S-18) shows the water absorption for the low and high void contents as a function of pressure. At atmospheric pressure and at 13,300 psi there is no significant increase in water absorption for the low void content material. For the high void content material, there is a gross increase in the amount of water absorbed at atmospheric pressure, and a tremendous increase at a high pressure where the water can be forced into the laminate. This may be analogous to some of the work that is being done in the high temperature applications where under high temperature one finds the higher water pickup.

Work was also directed to the effect of fatigue on S-glass epoxy materials. (S-19) At 10,000 cycles, r equal 0, in interlaminar shear fatigue, a small sample, which is 4 inches by a half-inch by a quarter-inch thick. For a 2 inch span, it is observed that there is a decrease in the dry fatigue strength, and a much more rapid decrease in the fatigue strength in the wet mode. The fatigue cycle was 30 minutes at pressure, followed by a 10-second decrease to zero load. In the wet mode the samples were completely immersed in water in the test chamber.

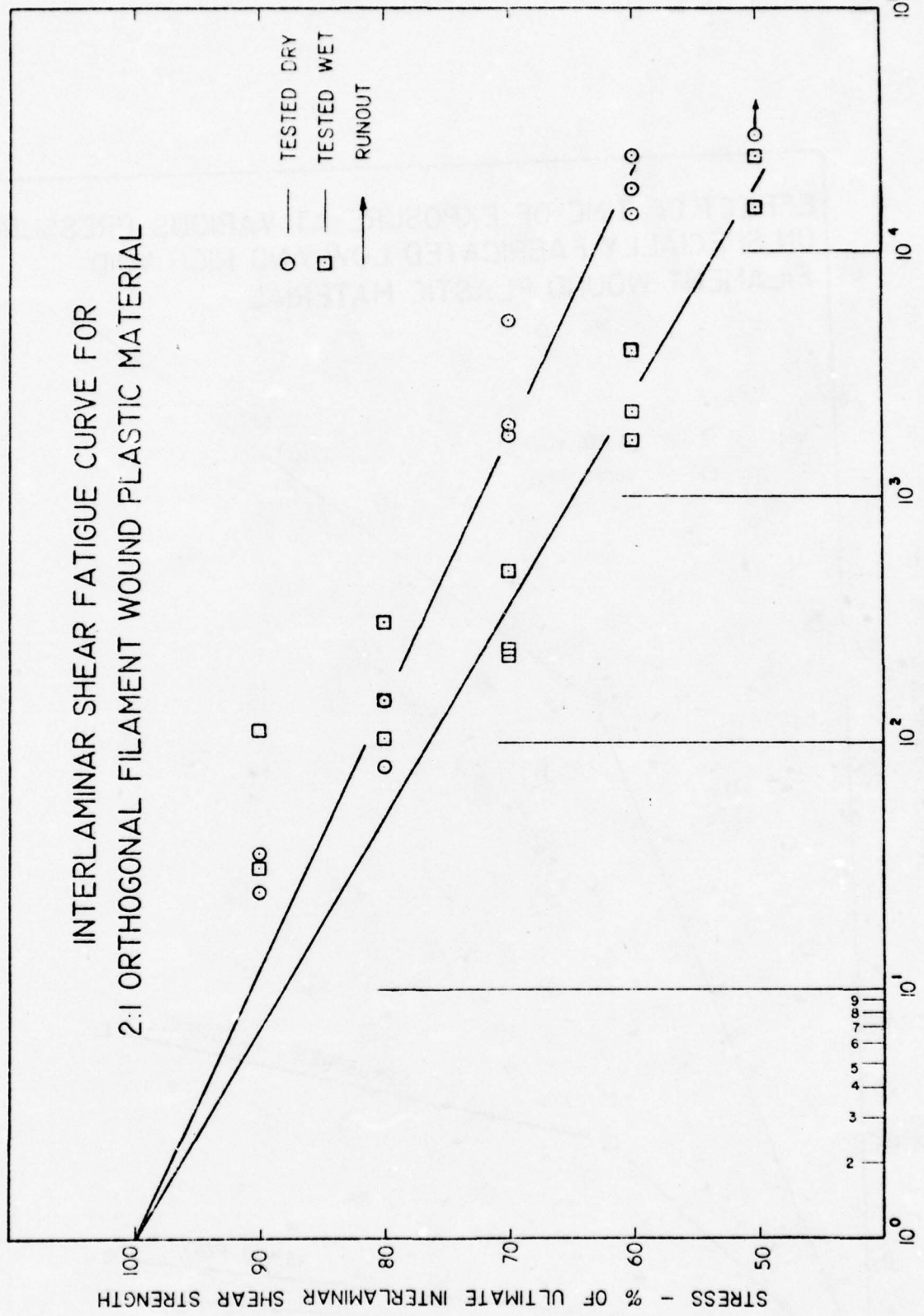
Simultaneously, an effort was also being directed



S-18

DTNSRDC

INTERLAMINAR SHEAR FATIGUE CURVE FOR 2:1 ORTHOGONAL FILAMENT WOUND PLASTIC MATERIAL



N - NUMBER OF CYCLES

S-19

DTNSRDC

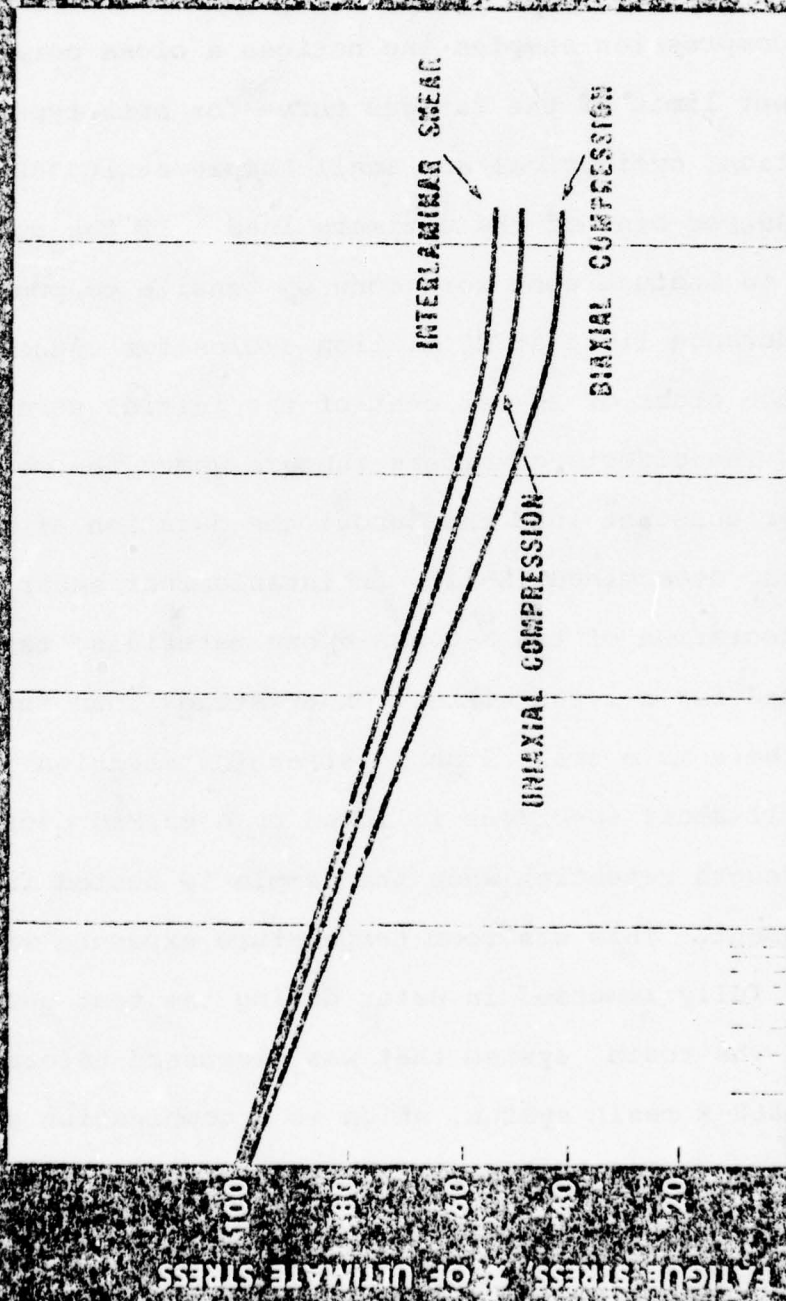
toward determining the fatigue strength of cylindrical models of similar configuration to the small samples. (S-20)

If we compare the results of the cylindrical samples subjected to biaxial pressure to the fatigue results on the small compression samples one notices a close correlation. The lower limit of the fatigue curve for both types of configuration, cylindrical and small sample at 10,000 cycles was about 40 per cent of the ultimate load. If the curve is continued to include some work done on tensile coupons one finds the endurance limit at 10 million cycles for these materials is in the order of 25 per cent of the initial strength.

The effects of stress rupture where the material would be under constant load throughout the duration of the test were also determined. (S-21) In interlaminar shear, the same 2:1 orientation of the S-glass epoxy materials, tests were conducted for a 1,000 hours. Under steady load for 1,000 hours there is a small loss in strength retention in air of the small shear specimens followed by a marked decrease in the strength retention when the sample is tested in the wet environment. This was room temperature exposure with the samples fully immersed in water during the test period.

The resin system that was discussed before was the Shell 5868-R resin system, which is a combination of Epon 828 and the solid 1031 resin hardened with the nadic methyl anhydride and benzyldimethylamine. A similar study was conducted to determine the effect of resin on properties of composites subjected to extended immersion in water, (S-22).

S-N CURVE FATIGUE STRESS AS PERCENTAGE OF ULTIMATE

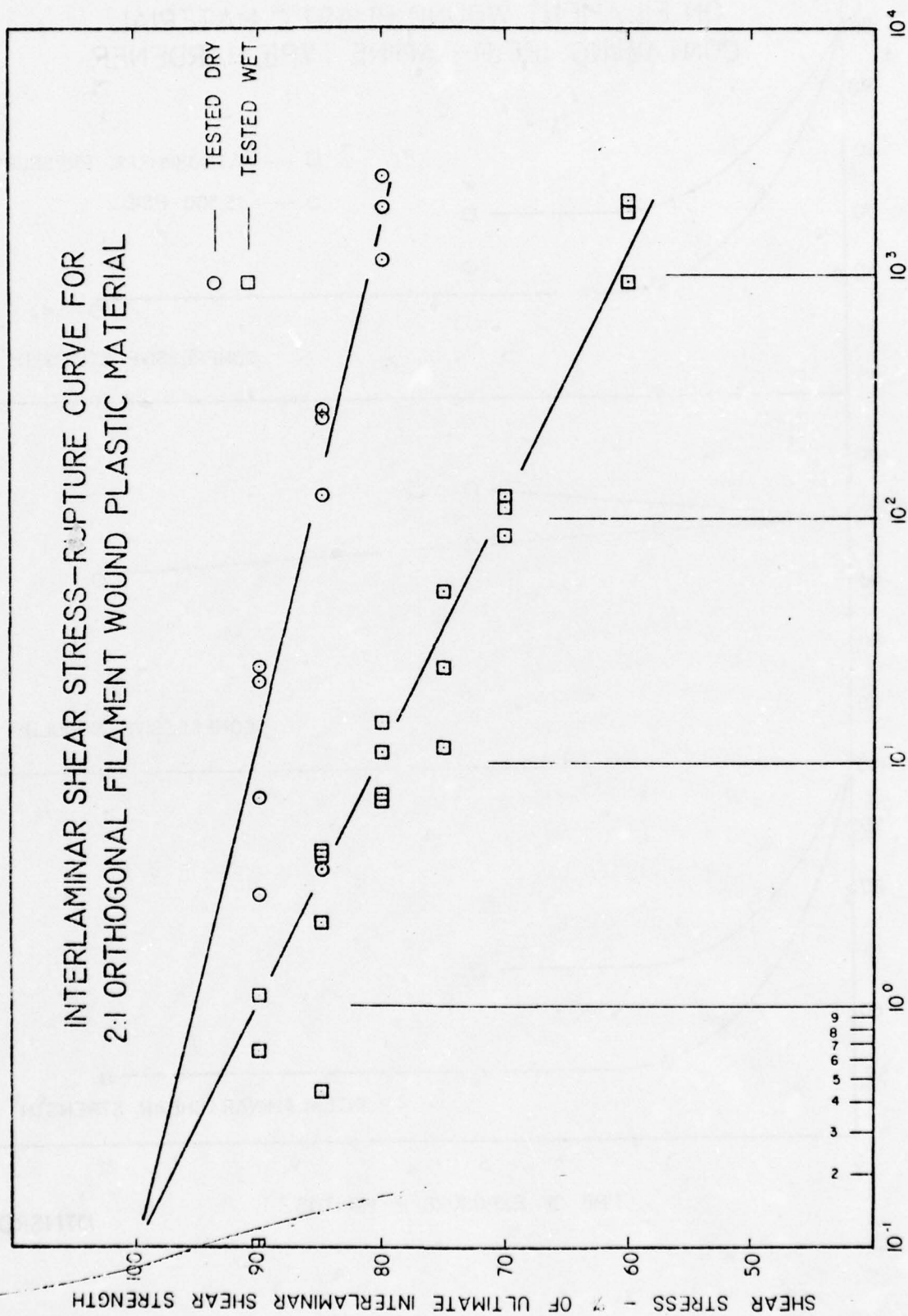


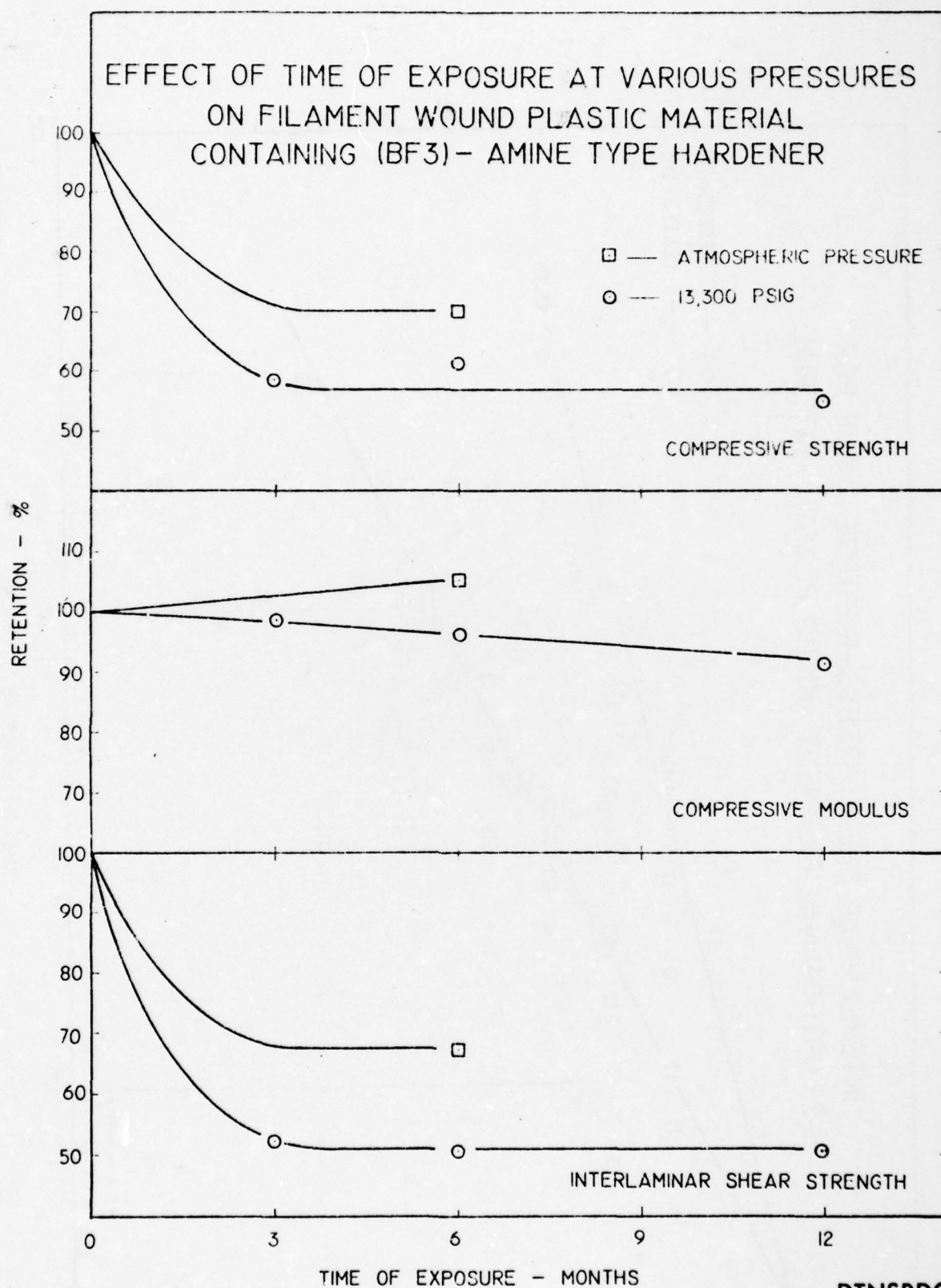
S-20

DINSRDC

DTNSRDC

S-21

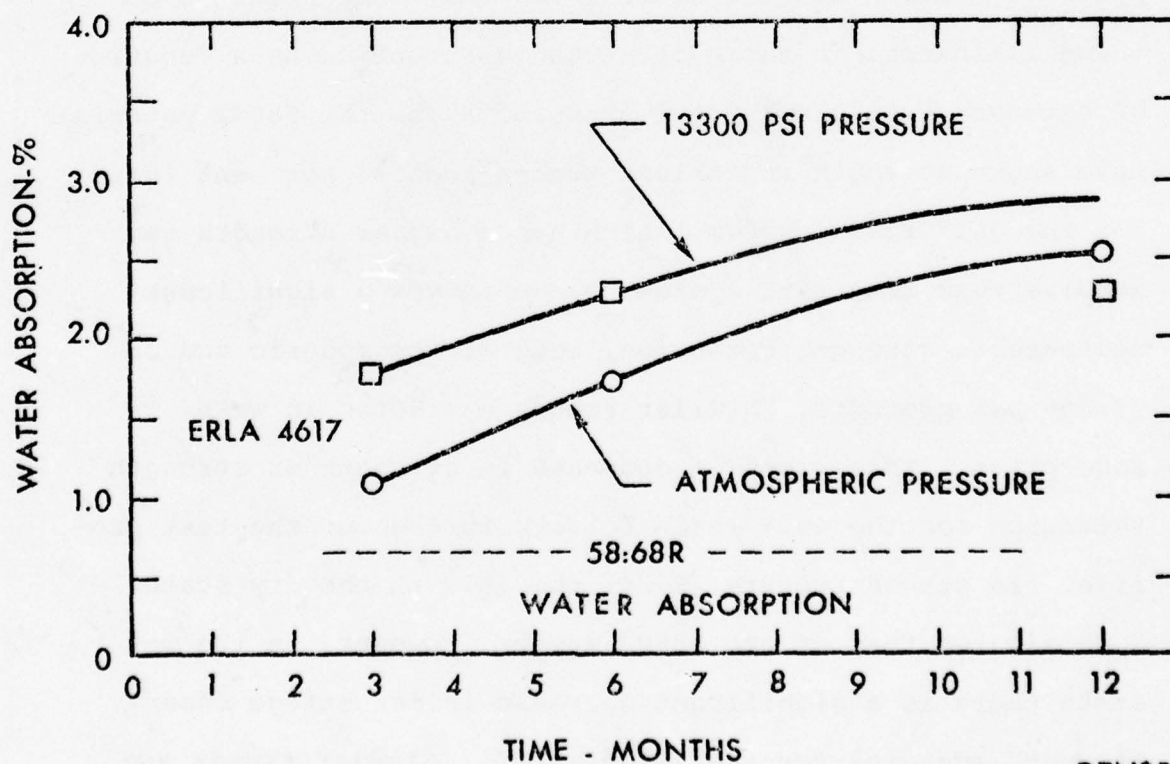
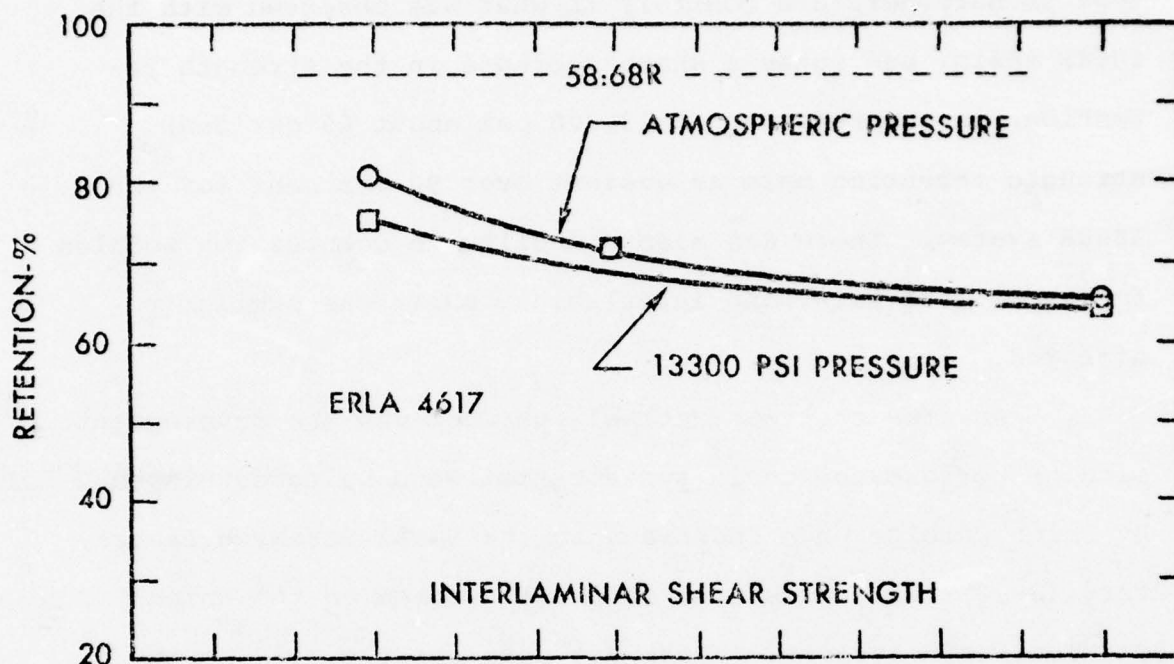




This is a conventional epoxy which contained a BF3 type of hardener, and contrary to what was observed with the 5868R resin, one notes a sharp decrease in the strength retention, in compression, at 13,300 psi about 65 per cent strength retention here as against over 90 per cent for the 5868R system. There was also a decline in compression modulus for these materials, and interlaminar shear was similarly affected.

An area that was actively pursued was the development of high performance resin systems that were being developed by Union Carbide under contract to the Naval Research Laboratory. (S-23) Laminates were fabricated based on the Union Carbide resin systems. These are data for the 4617 resin system. One can see the differences that were obtained on these laminates, in terms of strength retention as a function of extended exposure. Previous results for the 5868R material have shown strength retention greater than 90 per cent while for the 4617 resin system, which has a higher strength and modulus than the 5868R system, one observes a significant decrease in strength retention, both at atmospheric and at 13,300 psi pressure. Similar trends are noted in water absorption. This trend of decrease in strength or strength retention for the 4617 resin follows throughout the test profile. In stress rupture, (S-24) the 4617 in the dry state approximates that of the 5868R system, however, in the wet state there is a significant decrease in percentage shear strength sustains for the 4617 system. Similar trends are

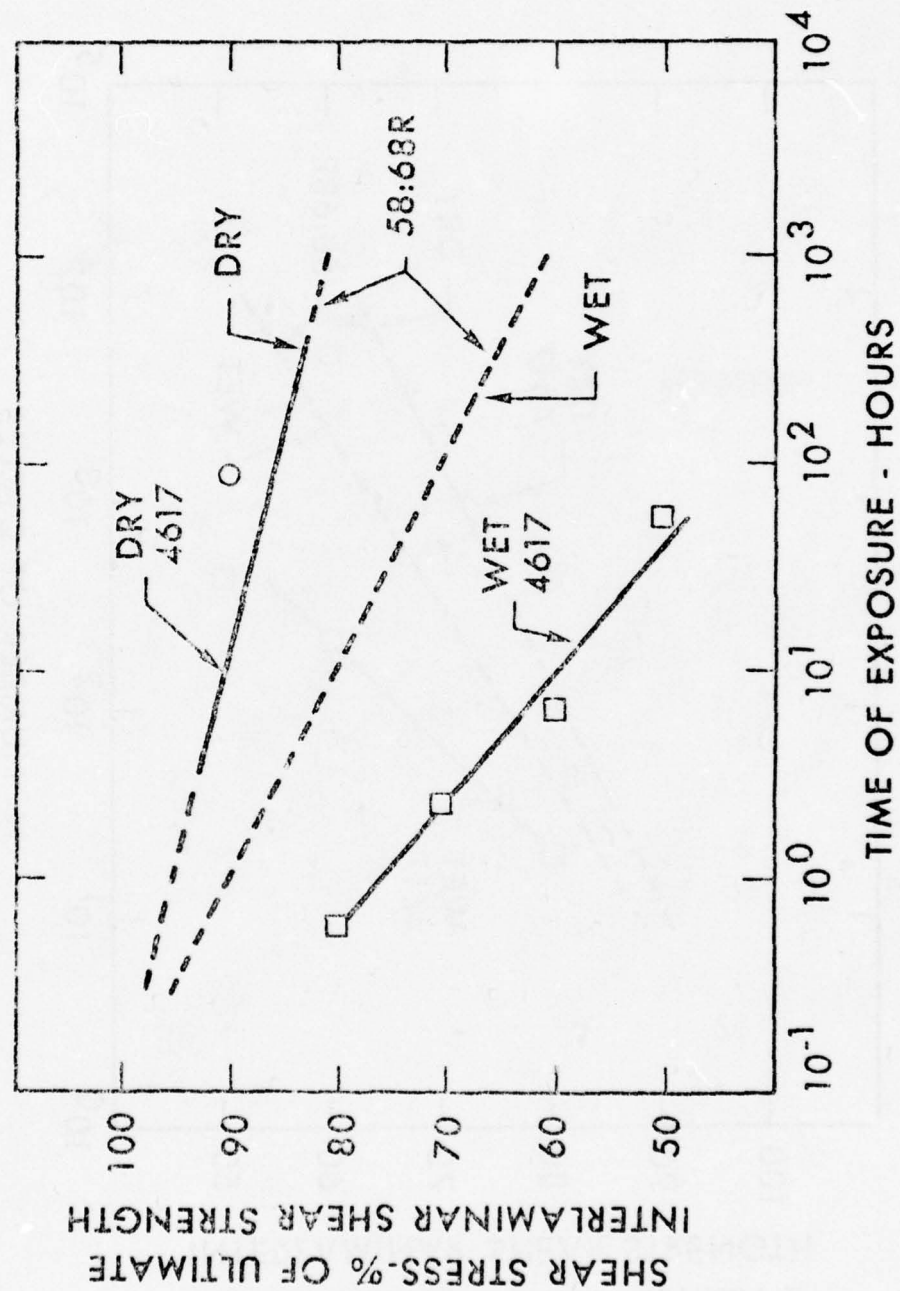
EFFECT OF WATER ON ERLA 4617 FWP COMPOSITE



S-23

DTNSRDC

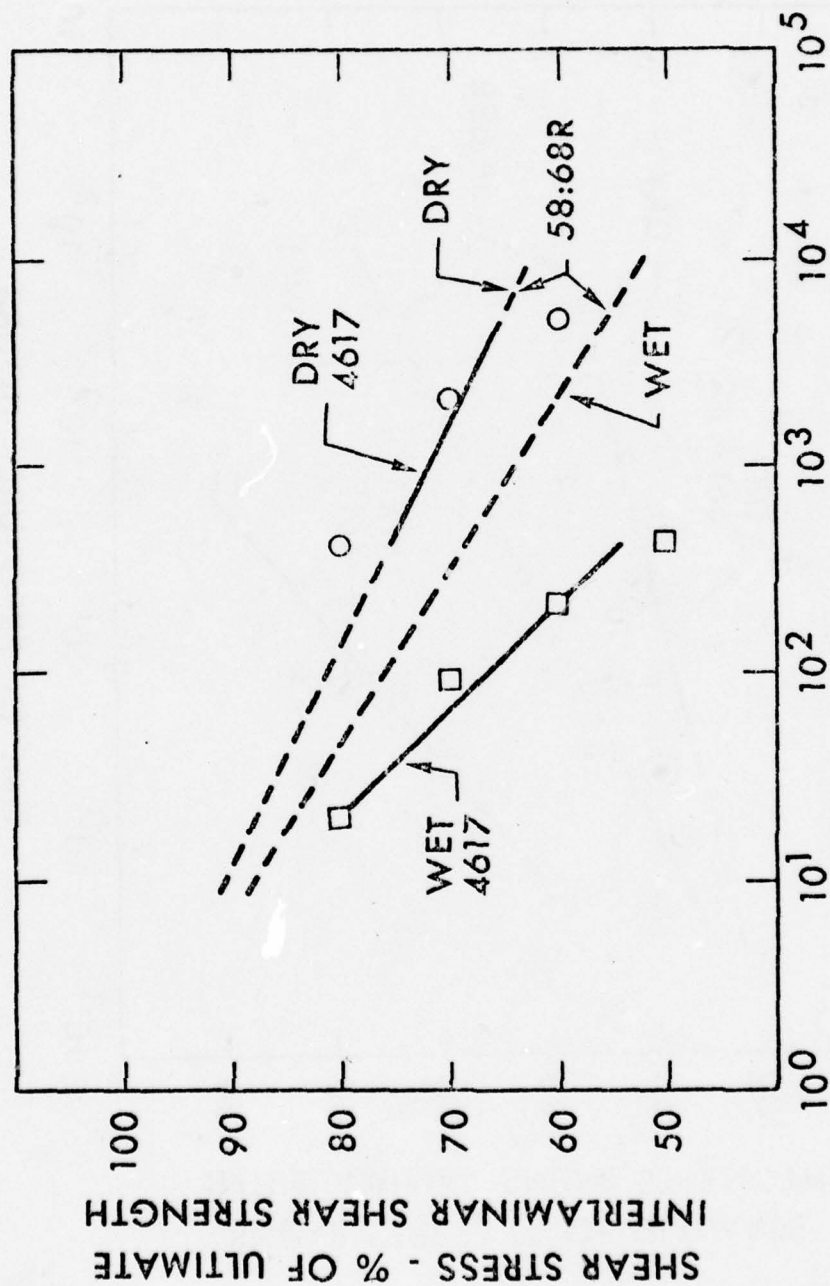
EFFECT OF STRESS RUPTURE ON ERLA 4617 FWP COMPOSITE



DTNSRDC

S-24

EFFECT OF FATIGUE ON ERLA 4617 FWP COMPOSITE



N- NUMBER OF CYCLES

DTNSRDC

S-25

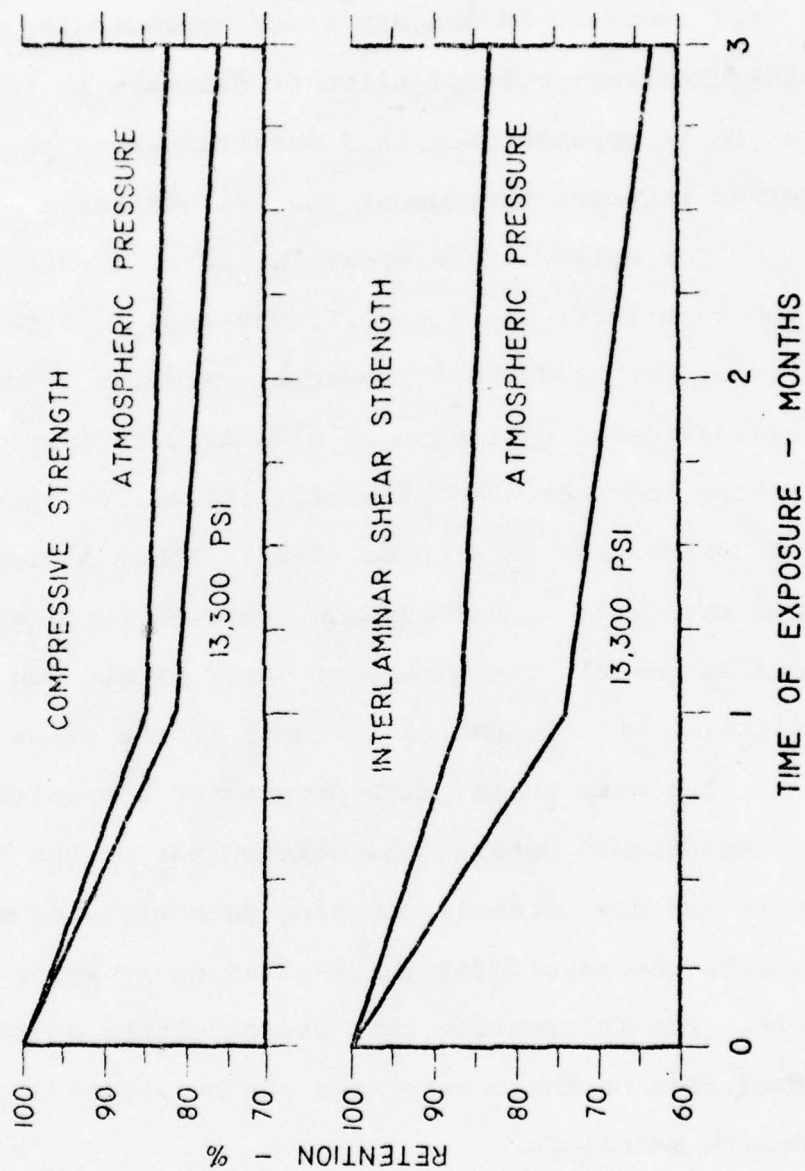
observed in fatigue. (S-25) In interlaminar shear, with the samples immersed in water throughout the fatigue cycle, with the same type of cycle that was used for the 5868R materials, the 4617 laminate in the dry state approximates that of the 5868R. However, more significant decrease in the fatigue strength is apparent for this material where the sample is immersed in water throughout the fatigue test.

For hollow glass-epoxy laminates (S-26) it was observed that there was a significant loss in strength at atmospheric and at 13,300 psi pressure. Similar trends were noted in evaluation of cylinders of similar materials. Significant increases in water absorption for the hollow glass materials at both pressures were noted. (S-27) These increases were higher than what we had experienced with the S-glass-epoxy materials. (S-28) The amount of water pickup was directly proportional to the volume of the void in the glass fiber.

The deep submergence program on composite materials was discontinued because the development of the HY-130 materials and the recently emerging technology of welding titanium. This made the payoff for the S-glass epoxy materials no longer viable. The information that was developed on the effects of immersion on these materials can be applied to the advanced composite materials.

Advanced composite materials, particularly graphite epoxy are being actively considered for high performance ship applications, particularly for hydrofoils. This is a typical hydrofoil with two foils, one foil forward and one foil aft.

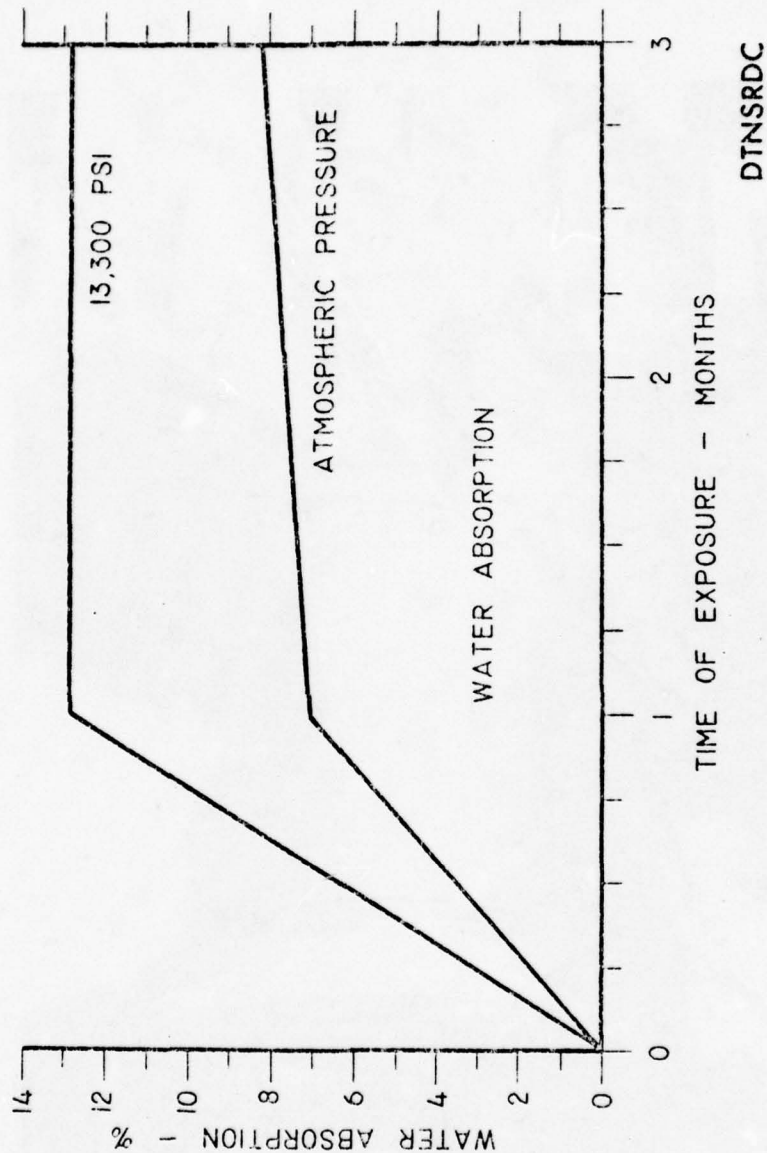
EFFECT OF WATER ON STRENGTH OF HOLLOW GLASS FILAMENT WOUND EPOXY LAMINATES



DTNSRDC

S-26

WATER ABSORPTION OF HOLLOW GLASS FILAMENT WOUND EPOXY LAMINATES



DTNSRDC

S-GLASS EPOXY FILAMENT WOUND PRESSURE MODEL



COPY AVAILABLE TO DDC DOES NOT
PERMIT FULLY LEGIBLE PRODUCTION

DTNSRDC

S-28

These materials are also being considered for ACVs, and other fast boats of the future Navy. There have been a number of studies conducted on the use of advanced composites to determine what the payoff will be for hydrofoils, of 1,000 and 2,000 ton weight. The significance of the weight of the foil section becomes quite apparent. In order to induce lift in the boat, the foil has to be of such a size that propulsion equipment at the current time is just not available to lift the ship out of the water and be foil born. The only way that this can be accomplished is by reducing the weight of the foil section or reducing the weight of the ship's structure.

The most probable area for successful application of composite is the strut/foil and that is why the current Navy philosophy is to utilize graphite epoxy materials for hydrofoil applications. These are potential payoffs in these applications. In one hydrofoil the steel strut system would weigh 53 per cent of the structural weight of the whole ship. If graphite epoxy was used it would only weigh some 29 per cent of the ship's structural weight, (S-29).

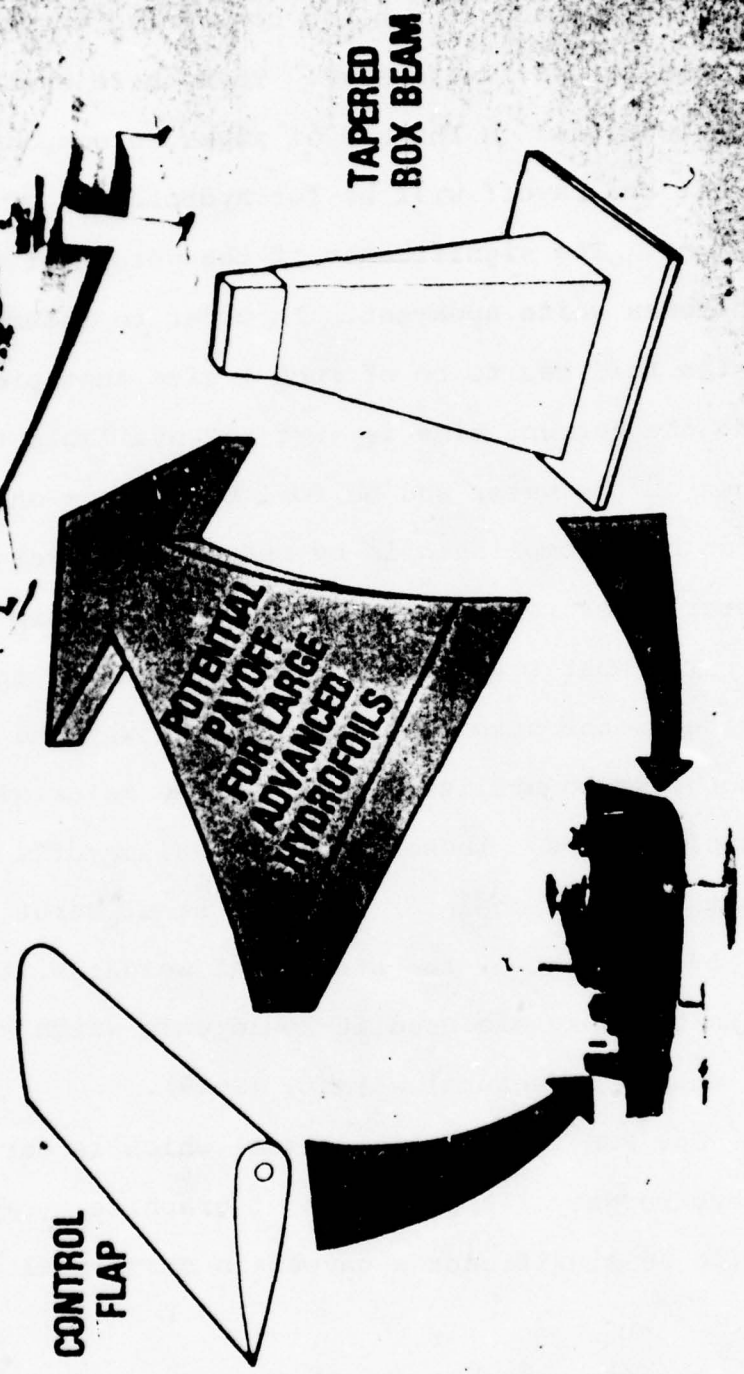
The PCH is a smaller vessel which is currently being used by the Navy. Application of graphite epoxy would not result in as significant a payoff in structural weight reductions.

Current programs are being addressed to the design and fabrication of a box beam, which is an element of a foil, and the control flap, which is aft of the rear foil. There are two contractual efforts directed toward the utilization

ADVANCED COMPOSITE STRUCTURAL COMPONENTS FOR STRUT/FOIL SYSTEMS OF ADVANCED HYDROFOILS

STEEL STRUT/FOIL SYSTEM = 53% STRUCT. WGT.

FRP STRUT/FOIL SYSTEM = 29% STRUCT. WGT.



STEEL STRUT/FOIL SYSTEM = 21% STRUCT. WGT.

FRP STRUT/FOIL SYSTEM = 13% STRUCT. WGT.

of these two elements. The box beam, which will be fabricated soon will be tested in fatigue and compared with the existing data base that has been generated on steel box beams of similar constructions. The control flap which will be fabricated will be installed on the PCH and in-service data will be developed.

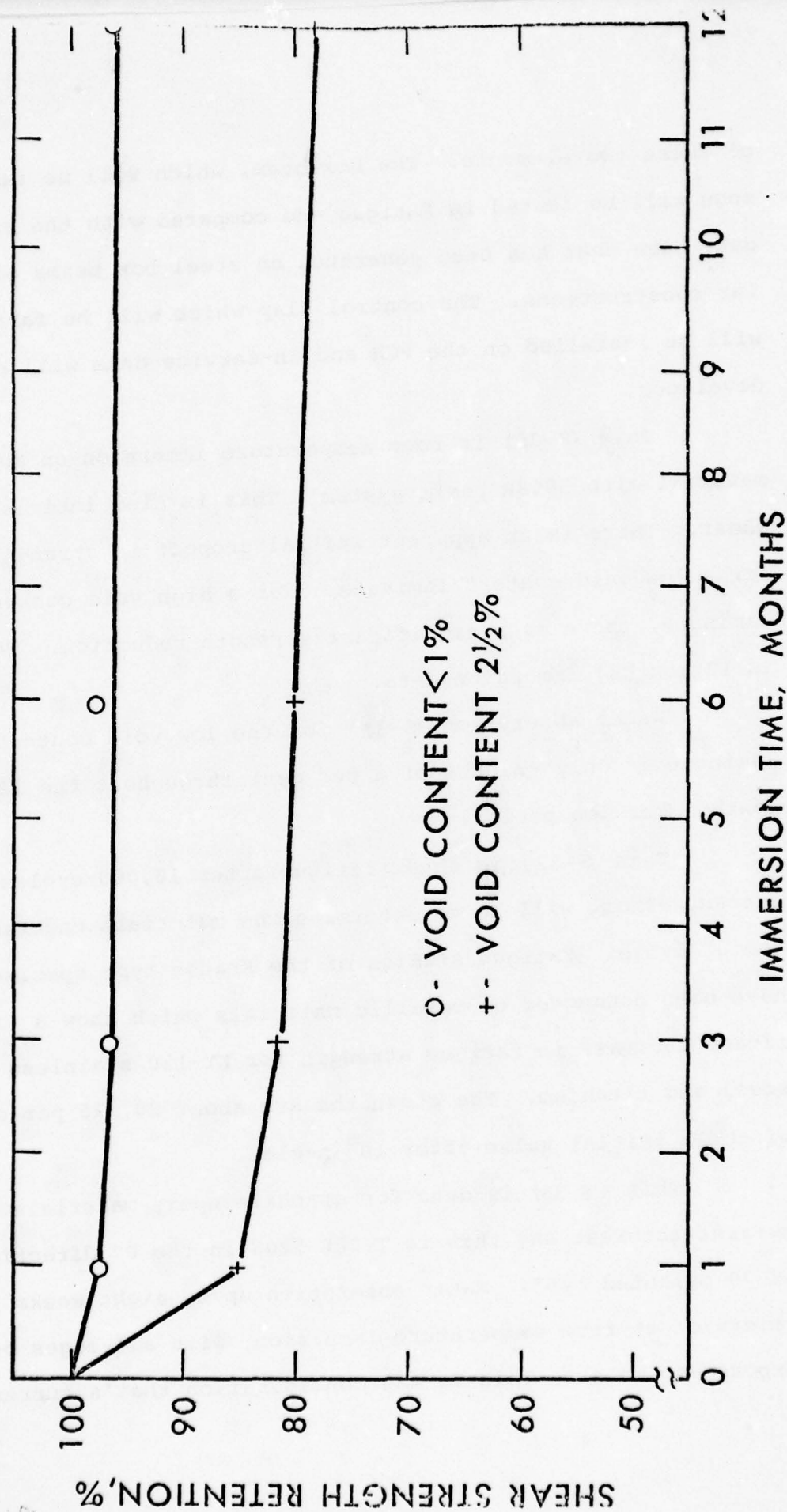
This (S-30) is room temperature immersion on Modmor-2 material with 5868R resin system. This is also interlaminar shear. There is an apparent initial dropoff in strength for a low void content laminate. For a high void content laminate, there is a significant strength reduction. This is 12 months' immersion data.

Water absorption (S-31) for the low void content laminate is only 4/10ths of a per cent throughout the 12-month immersion period.

This (S-32) is shear fatigue after 10,000 cycles, current effort will be to determine the materials endurance to 10^8 cycle. Fatigue studies of the Krause type specimen have been conducted on metallic materials which show a significant decrease in fatigue strength for HY-130 stainless steel and titanium. The strengths are about 20, 25 per cent of their initial value after 10^8 cycles.

This (S-33) is data for graphite epoxy materials of current interest and this is T-300 5208 in the 0° direction GY-70 oriented $\pm 45^\circ$. Water absorption up to eight weeks immersion at room temperature immersion, with all edges being exposed to water. This is the configuration that's currently

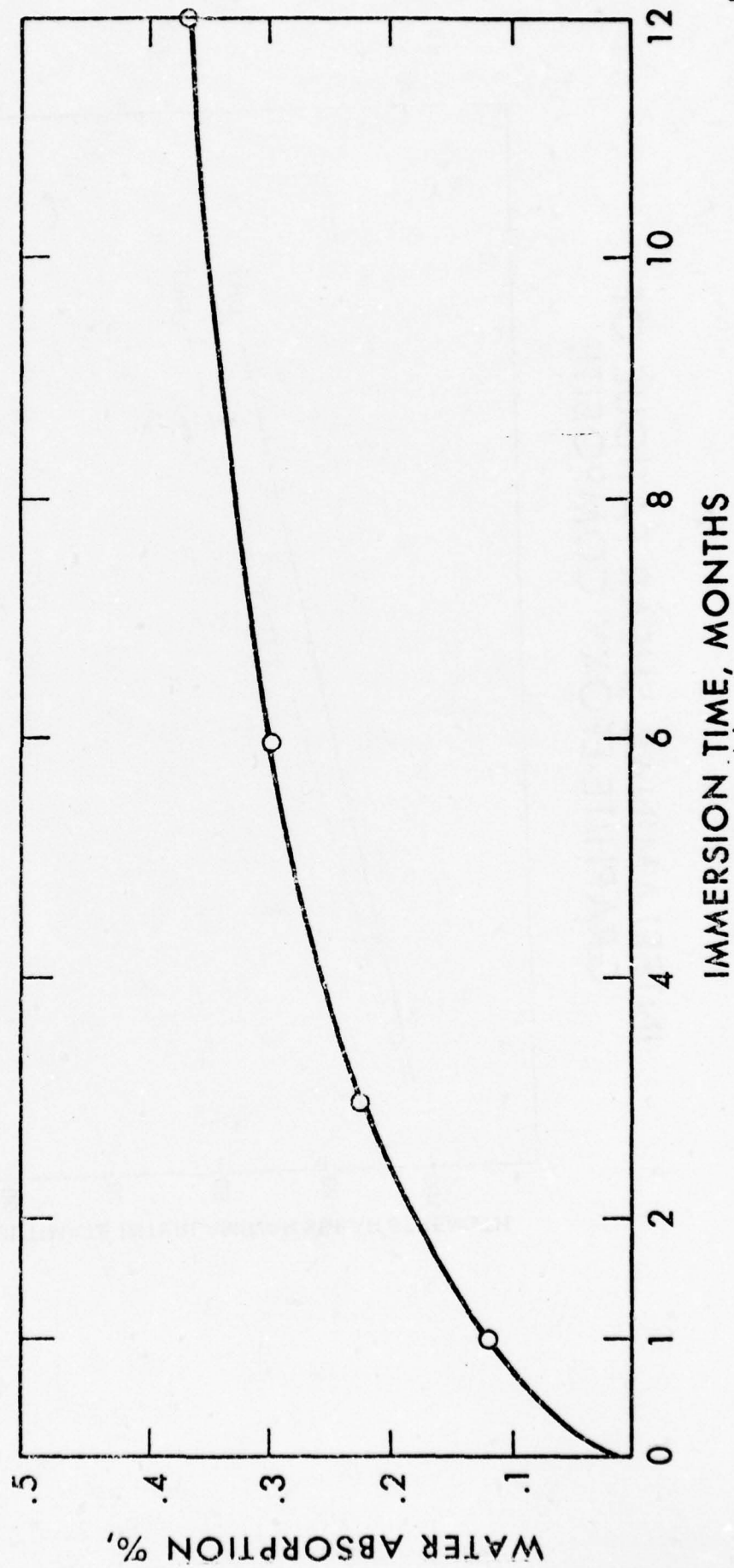
EFFECT OF IMMERSION IN WATER AT ROOM TEMPERATURE ON INTERLAMINAR SHEAR STRENGTH



S-30

DTNSRDC

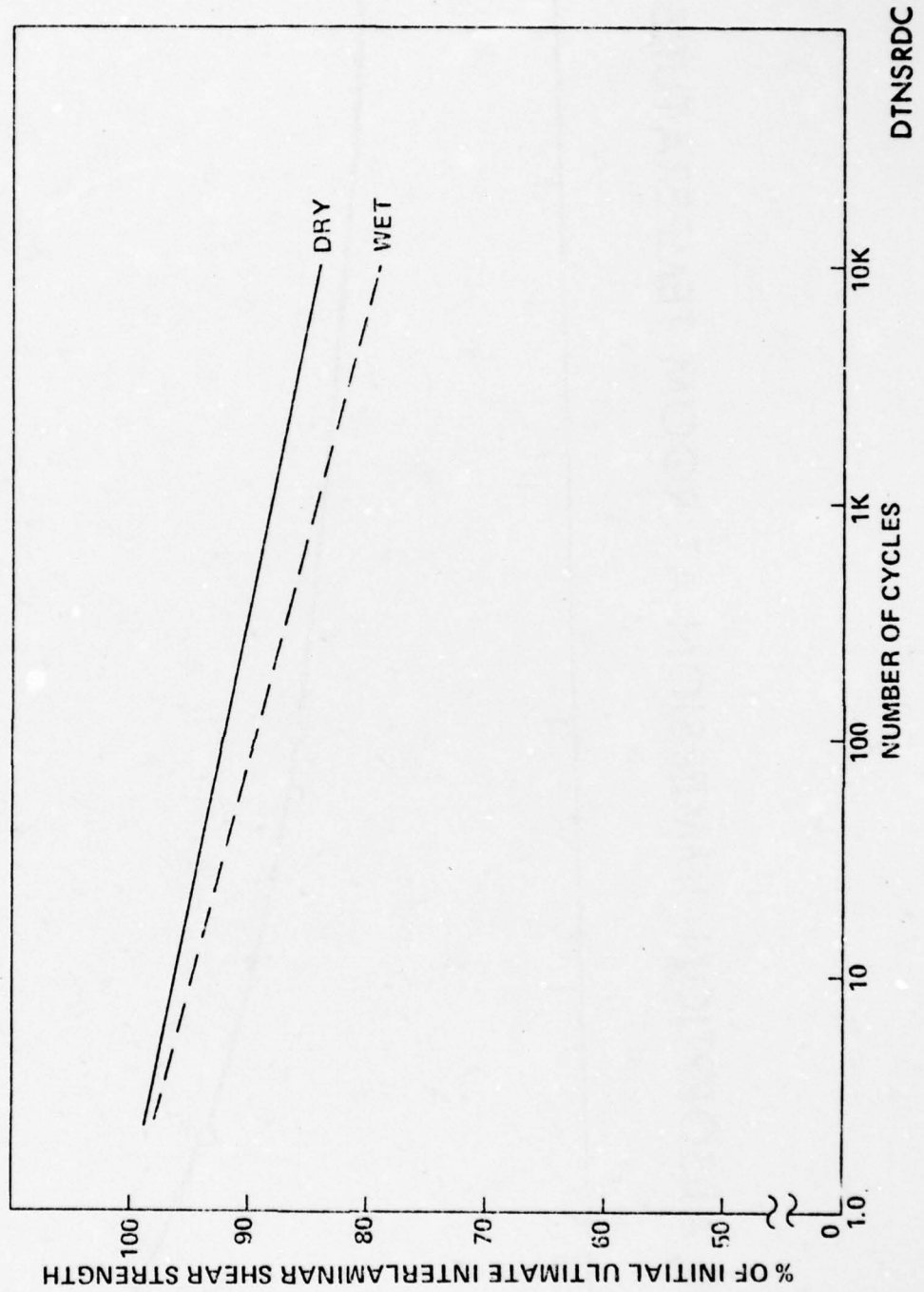
WATER ABSORPTION; IMMERSION AT ROOM TEMPERATURE



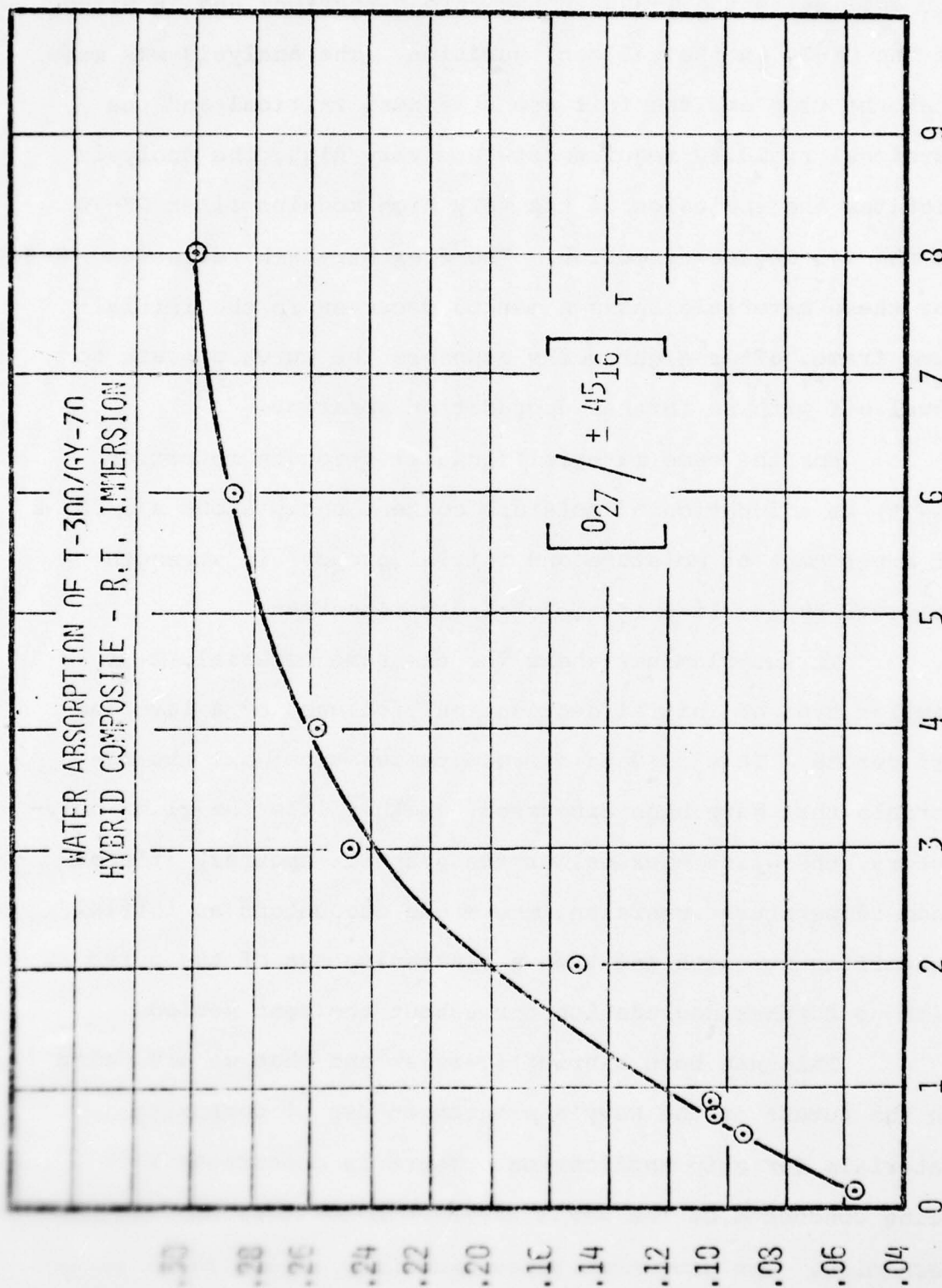
DTNSRDC

S-31

INTERLAMINAR SHEAR FATIGUE OF GRAPHITE-EPOXY COMPOSITE



S-32



IMMERSION TIME, WEEKS

DTNSRDC 167

S-33

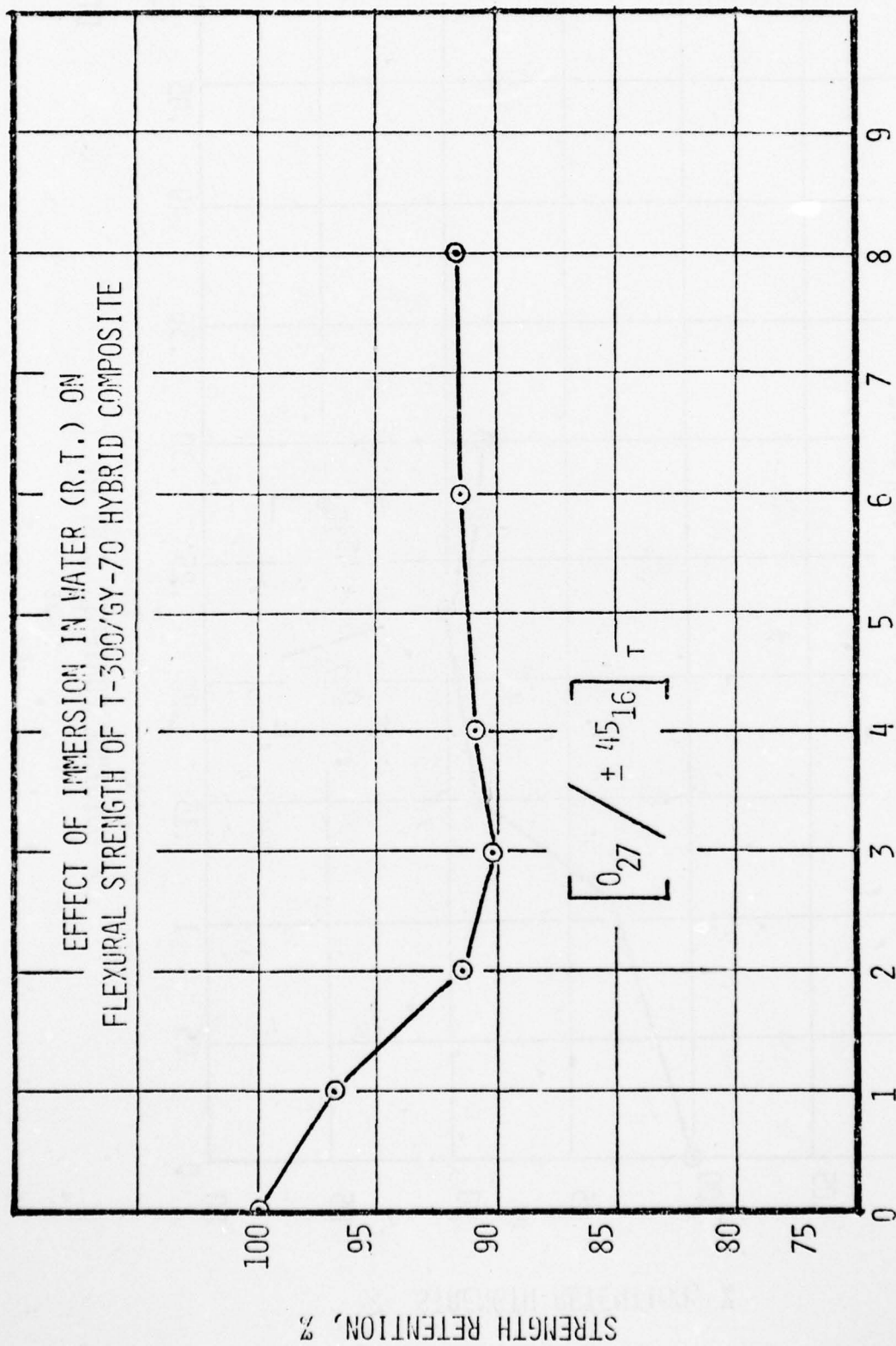
being addressed for the box beam effort, the orientation is 0_{27} applies to the T-300 in the zero directions and 16 plies of the GY-70 in the ± 45 configuration. The analysis was made that the flap and the foil are stiffness critical and the torsional rigidity requirements are very high, the analysis dictates the inclusion of the very high modulus fiber GY-70 in the ± 45 degree direction. The flex strength retention (S-34) for these materials shows a marked decrease in the initial time frame, after eight weeks exposure the curve appears to level off with no further degradation apparent.

For the same material flexural strength retention (S-35) as a function of moisture content shows about a 3/10ths of a per cent of moisture and initial dropoff in strength followed by leveling off in strength retention.

In interlaminar shear for the same material, (S-36) a similar type of initial degradation, followed by a leveling off period. This is data at room temperature; all the materials that have been discussed, whether it's the glass polyesters, the glass epoxies, or the graphite epoxies, it's at room temperature immersion, where one encounters an initial dropoff in strength and then a flattening out of the curve with no further degradation throughout the test period.

This has been a brief overview and what we are doing in the future of the Navy's program on use of composite materials for ship application. There is concurrent work being conducted at the Naval Research Laboratory on fracture mechanics. The Navy structures community of the David Taylor

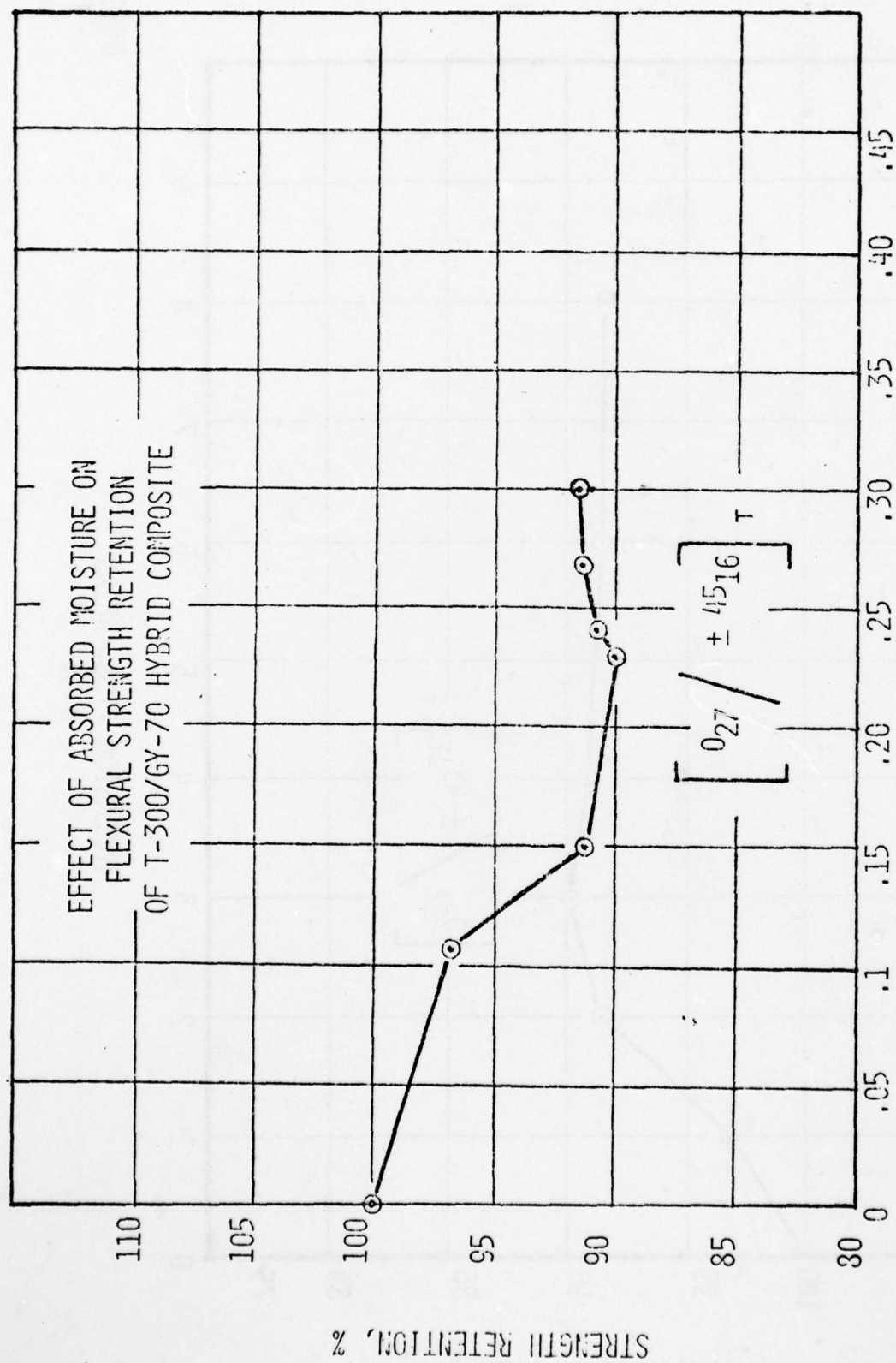
S 25



DTNSRDC

IMMERSION TIME, WEEKS

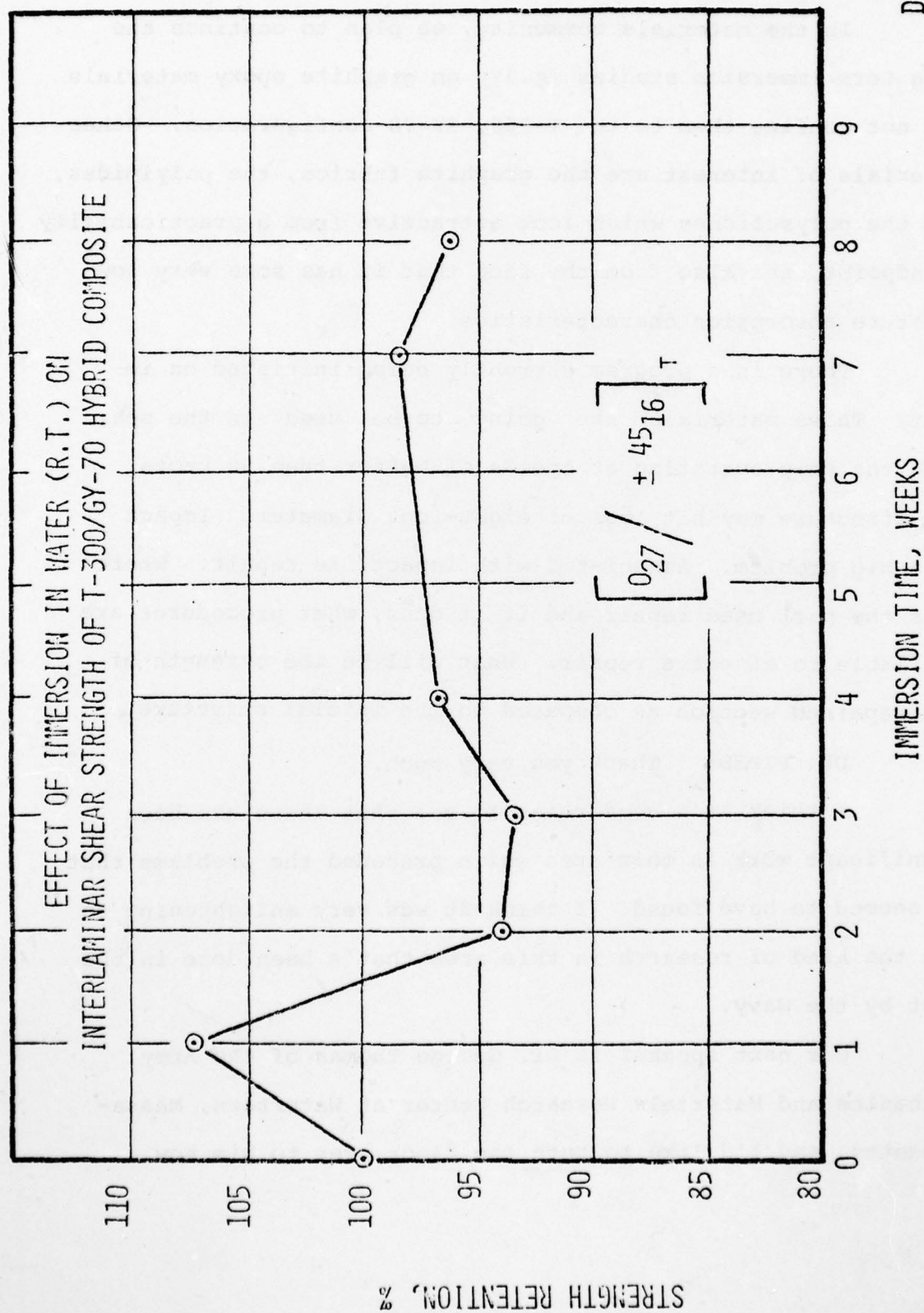
S-34



MOISTURE CONTENT, % BY WT.

DTNSRDC

S-35



DTNSRDC

S-36

Naval Ship R & D Center will do the structural evaluation of the box beam and in-service evaluation of the foil flap.

In the materials community, we plan to continue the long term immersion studies (S-37) on graphite epoxy materials and not confine them to the T-300, GY-70 configuration. Other materials of interest are the graphite fabrics, the polyimides, and the polysulfones which look attractive from a practicability standpoint, and also from the fact that it has some very low moisture absorption characteristics.

There is a program currently being initiated on impact. These materials are going to be used in the sea, with the ship operating at speeds of better than 50 knots. The structure may hit logs of eight-foot diameter. Impact is a big problem. Associated with impact, is repair. Where does the part need repair and if it does, what procedures are available to effect a repair. What will be the strength of the repaired section as compared to the initial structure.

DR. PIPES: Thank you very much.

I think it's comforting to see that there has been significant work in this area which preceded the problems that we seemed to have found. I think it was very enlightening to see the kind of research in this area that's been done in the past by the Navy.

Our next speaker is Dr. George Thomas of the Army Mechanics and Materials Research Center at Watertown, Massachusetts, and I'd like to turn the floor over to him now.

FUTURE WORK

- DEVELOP STATIC AND FATIGUE DATA ON LONG TERM IMMERSION OF ADVANCED COMPOSITES AND JOINED SECTIONS
- DEVELOP IMPACT DATA NORMAL AND PARALLEL TO FIBER DIRECTION. CORRELATE DAMAGE WITH NDE.
- DEVELOP FAILURE CRITERIA BASED ON FRACTURE MECHANICS CONCEPTS
- DEVELOP ON-SITE REPAIR PROCEDURES
- CONDUCT AN IN-SERVICE EVALUATION OF FOIL FLAP
- CONDUCT FATIGUE STUDY (DRY & WET) ON COMPOSITE BOX BEAM CORRELATE RESULTS WITH EQUIVALENT ALL METALLIC BOX BEAMS.

DTNSRDC

2. Army Programs

DR. THOMAS: My name is George Thomas, I'm from the Army Materials and Mechanics Research and I'm glad to be here today to hear the apparent manics and depressives on the subject of moisture vapor transmission.

I'm both a manic - I'm a manic-depressive myself, so bear with me. I think I'm in the right place. The Army has a helicopter program which is dedicated to fiberglass rotor blades, and notice I said it's going to be fiberglass and not graphite, and that is a basic difference between us and the Air Force. At this point we go to the cheaper materials because we can't afford the more exotic materials, apparently, I am told. We are going to be building these fiberglass rotor blades and they will be flying and there will be billions of dollars worth of these rotor blades in the service, no matter what I say here today. So the name of the game for us materials people is to get with the program and for the name of the game from the engineers is: "Jesus, listen to us once in a while". First slide, please.

Our program is dedicated to the prediction and prevention of deterioration, and this field - next slide please, - was in such a mess when we started out, I had to start all over again and just my name is Thomas and I'm a doubting Thomas on this particular day. I am going to talk a little bit about the background characteristics, the exposure sites. Despite the

fact that the learned gentleman said we knew enough about them. I think we did know enough about them, but I just wanted to reassure myself and I will show you some data that's beautiful data. You won't have to be bored with straight lines for the rest of the morning.

Here is some data, we are comparing exposure sites, and we were assured by everybody that all the exposure sites all over the world were exactly identical, until we got on one composite we got a value of minus 8.9 per cent degradation, and when the votes came in from the grassroots there was minus 52 and minus 49 per cent, which is much higher degradation than any other exposure site.

So the 1-to-1 correlation of exposure sites was called a question at that point in time.

Next.

The problem of the test material for stress -- after this one, that one. Again, how do you test the material? We put it out in an exposure site in a prestressed condition, and you will notice that the degradation in CS, which is the prestressed one, is twice the degradation on the C, which is unprestressed, but otherwise precisely identical.

Next one.

This slide you can't possibly read, and I hope you can't read it because you may find some errors in it. What it says is there is one machine unpainted and stressed, painted, unpainted, machined, unmachined, stressed and prestressed

samples out in exposure, and I can prove by selecting my data that prestressing, painting, and machining does a composite good, and I can prove by selecting another point on this chart that doing exactly the opposite also does good, and I can prove any combination is good or any combination is bad by this slide.

Skip that one.

Okay. You take out -- well, these are the exposure sites that we chose. I have not been through all of them. I have been only to one in Australia, and that is a delightful trip. I recommend it highly. And, you know, we have Panama Canal Zone, we owned that at one time; Maynard, Massachusetts, Puerto Rico was chosen as an alternate to the Canal Zone and we got the benefit of one site in Germany. A friend of mine has U.S. stations at 36 places around the world. He does a good deal of traveling every year.

Next one.

Here's an exposing site outside of Maynard, Massachusetts, near my laboratory. You can see the racks where we expose things on that, and these are the data we collected from our Army meteorological teams. We paid attention to the solar energy, the temperature and the humidity in particular.

Next slide, please.

Here is the temperature curve, the ambient temperature is the lower one in the dots and the upper one is the top -- it's a tenth of an inch sample, about a tenth of an inch, and it's the front and the middle and the back of the sample measured by thermocouples. I put this one up because it's an

amusing one. The back surface is hotter than the front. This happened in Panama. It's quite reasonable, because this is evaporative cooling of moisture on the front surface of it. This shows, the last slide shows we went up to 120, this also shows it goes up to 120. This is in Maynard, Massachusetts, right outside of my backyard, and the other one is in Panama, which proves that Boston is a jungle.

Next slide.

We measured the radiation of the samples at Langley, and then we filtered out Langley into various discrete wave lengths, and the top band shows the total number of Langley received between the hours of 8 and 1800, which is eight in the morning and six in the evening.

Now, in July of '74, the UV is about 30.8. The UV in July is about 30.8 per cent of the invisible spectrum and in January it is 13.2 per cent. These spectra are not important. It simple tells you you have a cyclic amount of UV in the sunlight.

Next slide, please.

We also measured the relative humidity and at all of the stations as a function of time during the day, and for those of you who are interested in plotting the course of moisture vapor, please note that your temperature of your sample does change and the relative humidity does change, and this has to be taken into consideration.

We measured again this slide, we followed the Langley and the temperature and showed that lo and behold, yes the Langley did follow the temperature rise rather exactly.

Go ahead.

This is a solar energy integrator in which we pick up narrow bands in the UV and the visible.

Next slide, please.

We have plotted here the collective amount of UV, traditionally from 400 back and also through the rest of the visible spectrum. So we have a lot of data on UV as a function of the wave length. So, you know what wave lengths to look for in your research.

Okay. So much for the characterization of the weather sites. We found nothing abnormal in the weather sites. Now, we went to a manufacturer and got a standard sample made up by this normally reputable manufacturer and he gave us the exact composition of his resin. He gave us his processing conditions and he told us what his processing conditions were in the book. Unfortunately, the people out in the plant don't read those processing conditions, and I think one of the problems we have is to get the people in the engineering side or out in the manufacturing side to follow the prescriptions that are laid down for us so we know what we are dealing with.

Next.

That's a composition material. We had one foot square placques, and we were orderly in the way we cut our samples out,

and this simply proves to you that we are orderly. Those little squares are test samples.

We didn't disagree with the manufacturer's results in terms of these are the mechanical values, tensile, short beam, shear and flex.

Next.

This is a very interesting chart, which means absolutely nothing, and I will prove it in the next slide.

Here are the data plotted, and we had the courage to let the statistics and the computer plot straight lines, and I don't know what these straight lines actually do mean. What it shows basically is we got a hell of a lot of data scatter, lots and lots of data scatter. And then the next one we find that if we do a point-by-point plot we get a typical mishmash of data from our exposure sites, and this is the kind of information you get on a hell of a lot of glass fiber reinforced plastics. You know, you try to make sense out of some of this data and somebody says, "Oh, we got an edge effect", and one of my people is great on edge effects. "All we have to do is seal the edge". So boy, we seal the edge and we are all set. So the moisture could not come along the length of the fiber, edge of the fiber, through the edge of the material. And here you could see that as I showed you before we didn't mark the samples where they were on location, so take my word for it. This is close to the edge next and over on that side is towards the middle and at 12 months, yes, it degraded more on the edge, less and less and less in the

center, and this looked all right. And we tried six months; that looked a little -- just about as good. Then 18 months; then we tried 12 months.

Now, let's look at two more test sites as to what happened then.

Next slide, please.

So a disaster. I mean we went from order to chaos.

Next one. Next one, please.

Well, okay. What we did then was we decided that maybe what our problem was was that we didn't have good characterization of our materials, that we had uneven samples and our samples were not too well prepared, and we did x-ray analyses on them. We did find that normally unidirectional materials were about 5 degrees off, and we found some other interesting things about these samples.

Next.

We were able to follow the carbonyl by measuring the carbonyl content using ESCA, and here is the development of the carbonyl and the first 40 in the Rain Forest, and Maynard site, where we had equivalent UV formation, we did get an equivalent amount of carbonyl formation.

The UV degradation went about 80 angstroms and then stopped, but we were able to, using Fourier infrared spectroscopy, get total reflectance for fiber it should be about 8, and by measuring the reflector we were able to show that we were losing resin from the surface of the fiber as a linear function of time.

AD-A035 437

DELAWARE UNIV NEWARK CENTER FOR COMPOSITE MATERIALS

F/G 11/4

THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED TEMPERATURE ON CO--ETC(U)

DEC 76 J R VINSON, R B PIPES, W J WALKER

AF-AFOSR-2966-76

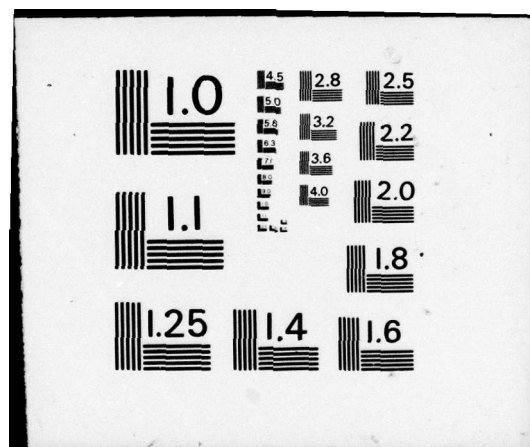
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We also used Fourier attenuated total reflectance, Fourier transforms, and we were able to show during the cure cycle how we were losing epoxy groups and gaining hydroxyl groups and gaining and losing functional groups, and we were able to follow the cure condition, the curing of a sample right through the end. And I think this is important, we were also able to use that technique in following the carbonyl formation out in the exposure site. So here is a technique that we think is useful.

We tried laser sputtering. What we did was hit it with a laser beam, collected the gases and then analyzed those gases.

This is the control up here. This is hit with the laser beam. That's the sample brought in from the field and then it was hit by the laser beam there. We collected the gases and, lo and behold, we did find a lot of effluent gases and they are listed on this slide. Please note that you get carbonyl types and hydrocarbons out of this particular exposure.

I don't quite understand why we get the hydrocarbons, but there they are, as a function of total months of exposure.

We also were able to show that, in these exposures, that the acetone, the plus group, went up and started to go over and the phenyl propane went up and is going, apparently accelerating as we go along.

When we follow it grossly, we find that the amount of exposure in the micromoles of the volume of gas you get off could correlate with the exposure time.

And an interesting finding, and there is a difficulty here in that the Rain Forest, where you have got very little UV, is still giving you off a lot of gases and we are looking back on our data, what we are finding, we think we are seeing, and in this game you can think you can see a lot of things, we think we are seeing more hydrocarbons coming off of the material that didn't get UV exposure.

We burned off the resins from the sample and found that resin loss was an easy thing to measure by burning it and weighing the glass afterwards.

One of the things we did with thermographic material analysis, gas chromatography and mass spectrometry, we analyzed the gases coming off, and we identified some gases that correspond to the aminosilane that was used as a coupling agent between the fiber and the matrix.

At the end of six months we were only able to find 60 per cent and 40 per cent respectively of that coupling agent. At the end of 12 months the coupling agent had completely disappeared from the sample in the form that it was there originally. It was an interesting finding and rather unexpected to us.

Now, you will recall that -- I had a graph that went like this for a gas analysis -- the gas went over. Now, if I flip it over, now I do the -- take the same laminate and measure the glass transition temperature you will see that the center, the center of the sample, maintains its glass transition temperature in these experiments with these resins. Now, that's all I can say is that with these experiments and these resins it stayed

about the same. But the top and the bottom, this is peculiar, because the bottom does not have the UV exposure, the top and the bottom the glass transition temperature seems to decrease. I think it's being confirmed in Australia, and it's not true of all the sites, unfortunately.

Now, this one, I have got this up here to remind myself that we simply used shims to measure the depth of the resin, and we sputtered out the resin down to the glass until we found glass and we found that our samples varied in surface gel coat, or whatever you want to call it, surface resin, from .4 microns to about 1.2 microns. The stress under a mass spectrometric analysis, this is a very interesting experiment to me -- we haven't followed it -- we are following it through, but under heat in mass spectrometry in a high vacuum we are able to find water, HF, and some monomer out of our original mixture, and when we test under tensile load and twisting load we found water, oligomers. I think this will be one of the most significant findings we have had as far as non-destructive testing, and how you cured your resin. We have been looking at the function of post-cure and how our post-cure may even be important. Cured in a forced air oven, UV exposure, the extent of oxidation as measured by carbonyl, used under the Fourier transform method, this is not ESCA, this is Fourier transform, you get a more rapid rate of oxidation or a carbonyl formation with -- when you post-cure in the air oven or you post-cure in vacuum you get a slower, and when you have an anti-oxidant there of course you get a slower rate.

Again, post-cure, this is zero and one and three hours on the thermomechanical analyzer. You can see again the change in glass transition temperature on the upper curve with the dip, one, two and three goes up, oh, I guess around 200 degrees there, the Rheovibron shows exactly the same kind of trend.

Now, it's interesting to note that since we are all together and the manufacturing people aren't here, let's get on their back today. When we had these samples cured it came to two hours before quitting time they'd let it go till the next day in the air oven. Now, we had instead of four hours prescribed cure, we had about 18. So that was one batch of samples. And then if it was three hours, they just turned the dammed oven off and quit. So we got anywhere between zero hours cure and 18 hours cure on the samples. And I would suspect that a lot of you have gotten exactly the same kind of samples, and I would make a plea for doing your samples yourself or having them done under conditions where you can watch them rather than have somebody who is anxious to get home to his wife because he has got to pay the gas bill.

Similarly, on moisture vapor it has been brought up on this set of resins, we found out that on the post-cure time that the moisture transport properties changed by a factor of 2 in this glass, from a unit of 6 down to 2. And we are not sure of the shape of this cure, but we will have that data at the next meeting of this body, if it ever meets again.

Next.

We have looked at accelerated weathering sites, and this

is the test site out in Arizona where they multiply the UV by mirrors and then maintain your sample at the same temperature and we found some rather good correlations from a chemical point of view, but not from a mechanical point of view.

Next.

From a chemical point of view, resin weight loss was good. These numbers are deceptive, 2.2 and 5.3, those are deceptive because your coefficient of variation is plus or minus 15.

Again, we found good correlation between the EMMAQUA site EMMAQUA stands for Equatorial Mirror Mount with Water. The water simulates the Panama Canal Zone or the tropics and your resin weight loss within coefficient variation of tenths, corresponds very well, your carbonyl corresponds very well; again, our mechanical properties didn't do well at all.

Next we showed some Kevlar and glass tubes we had been looking at. This is the result of the before and after exposure. Notice the gel coat on the upper one and the loss of gel coat below. We found that six months here corresponded to about five years, and this calculation was based simply on the loss of the resin from the surface.

These are the data from it. Very little change in the average burst strength, the top line there. It says there five to seven mills are lost from the surface, and there is enough mills on the surface to last you five years.

We looked into the problem of strains, internal strains in the composite, and here we have cut open a hoop a filament-wound hoop, and if that were completely relaxed it should just

lay in a perfect circle. It's not completely relaxed and didn't lay in a perfect circle.

Next.

Now, if you make a hybrid, which we are, in the Army, are looking at from a practical point of view of trying to use the higher-priced fibers, here we filament wound a tube and the two inner layers, the glass inner layer and the graphite, did about the same thing that they did on the previous slide, and the outside one was under tension obviously in the composite and spreads out. It's an interesting observation, and it shows, I think, that we are going to have to pay some attention to internal strains.

In conclusion, the first thing I'd like to say is I'd like to see, if I had a recommendation to make, a sort of a bureau of standards which could prepare the samples in a prescribed way so we could all be working on the same materials. I spent two years on this program. The only reason I've gotten away with this two years in the program is that no one in the Army believed me and they let me alone for two years. So I have been able to do the kind of work I described in developing diagnostic techniques.

The second is I think we can go a long way in developing a lot more diagnostic techniques, and, thirdly, I think that process control is really the key -- it's the key that the manic can predict that he is going to succeed. And lack of process control is the key that the depressive can prove that he is going to fail.

DR. PIPES: Thank you very much, George.

I was never quite sure whether you were saying manic or maniac, which might be more appropriate in some of our cases.

[Luncheon recess]

A F T E R N O O N S E S S I O N

D. Problem Areas

DR. VINSON: This morning we were given an overall outline of what the program is about, and also historical sketches on programs involved with the Air Force and the Army, the Navy, and one industrial firm. Now that everyone is up to date and understands the problem, this afternoon we will begin to address certain categories that tell in part what the problem is, and give some views of our guest speakers.

We have divided the categories into physical properties correlation models, characterization of constitutive properties, failure processes, test methods, and experimental research and non-destructive evaluation. This afternoon we will be listening to various people discuss their own views. We have tried to formulate this so that we get the views not only of solid mechanics specialists and also polymer chemists, and then as we see tomorrow morning we are going to divide into five different groups. As the afternoon progresses, if each of you will please decide in which of the five groups you would like to participate in the group meetings tomorrow in formulating a near-term and a long-range road map of what should be done. Please put your name under

the group that you would like to attend tomorrow, we will meet in five different smaller rooms tomorrow from 8:30 to 10:30 to formulate, the road maps in these five different areas.

I might mention that there will be a refreshment hour at 5:30 to 6:30 this afternoon, and following that we will have dinner, and this evening then we will resume at eight o'clock for the discussion of the AFOSR program and plans with Don Ulrich and Bill Walker.

Our session chairman this afternoon is a Professor of Material Science and Chemical Engineering here at the University of Delaware. As you heard before, our Center for Composite Materials involves professors in three of the four engineering departments and Roy McCullough, who has been here for five years, prior to that with Monsanto Chemical and Boeing - Seattle, and one of the very talented people in chemical engineering who form a part of our Center for Composite Materials. Roy.

DR. MC CULLOUGH: Thank you.

This afternoon's session is directed toward the physical properties characterization problems of the constitutive elements of the composite materials. After our talk before dinner, I think probably another workshop session should be in order, namely, a prayer session. Those of us that work with polymers are quite familiar with that technique in having solved some of our problems.

Our list of speakers this afternoon is rather long. All of them have something very important to say, and I think I will

immediately proceed with the meeting. I will try to keep rather tight tabs on the time, so I hope I don't offend anyone by standing up and hovering over them when they run over a little bit, because we have a very large schedule this afternoon.

Our first speaker is Dr. Kibler from General Dynamics, in Forth Worth, and I saw him just a moment ago.

1. Physical Property Correlation Models

DR. KIBLER: Put the first slide up, please (K-1).

I'm Ken Kibler from G.D. - Fort Worth, and I would like to talk to you about a selection of recent data that several groups at GD have recently obtained. I don't believe that most of this data has been seen by any of you yet.

Specifically, I would first like to talk about some physical modeling data which deals with swelling measurements and moisture absorption. That work was done by Lee McKague, John Halkias, and Jack Reynolds, whom you will be hearing from later. Next I will discuss work on absorption mechanisms in neat resins by Harris, Carter and myself, and finally some thermal spike results done by a new lab member, Ben Rodini, whom you may know from Drexel, and myself.

The first deals with physical modeling, and Figure 1 shows an exposure matrix to indicate the extent of the environments we have studied at GD, ranging from room temperature to 300 degrees, humidities from immersion down to 45 per cent, and various laminate stacking sequences. All the data is on 5208/T300 laminates or neat 5208 resin.

The second figure is a composite picture of essentially all the neat resin data over that entire temperature range, both immersion data and vapor phase data, weight gain versus change in specimen length. Since this is the longest dimension of the specimen, it represents probably the best measurements. All of the data, I think I can safely say, falls within the shaded area that I have indicated. For the total of these physical modeling measurements we are talking

EFFECTS OF MOISTURE AND ELEVATED TEMPERATURE
ON 5208/T300

K. G. KIBLER
GENERAL DYNAMICS/FT. WORTH

ABSORPTION MECHANISMS

H. G. Carter, Jr.
K. G. Kibler

PHYSICAL MODELING

E. L. McKague, Jr.
J. E. Halkias
J. D. Reynolds

THERMAL SPIKE EFFECTS

K. G. Kibler
B. T. Rodini, Jr.

FIG. 1 MOISTURE ABSORPTION AND DIMENSIONAL CHANGES

5208 RESIN AND 5208/T300

EXPOSURE MATRIX *

TEMP. (°F)	RELATIVE HUMIDITY (%)		
	45	75	98 IMMERSION
75	●	●	●
120			●
150	●	●	●
180			●
195			●
212			● *
240			● *
270			● *
300			● *

* Equilibrium Vapor

SAMPLE TYPES:

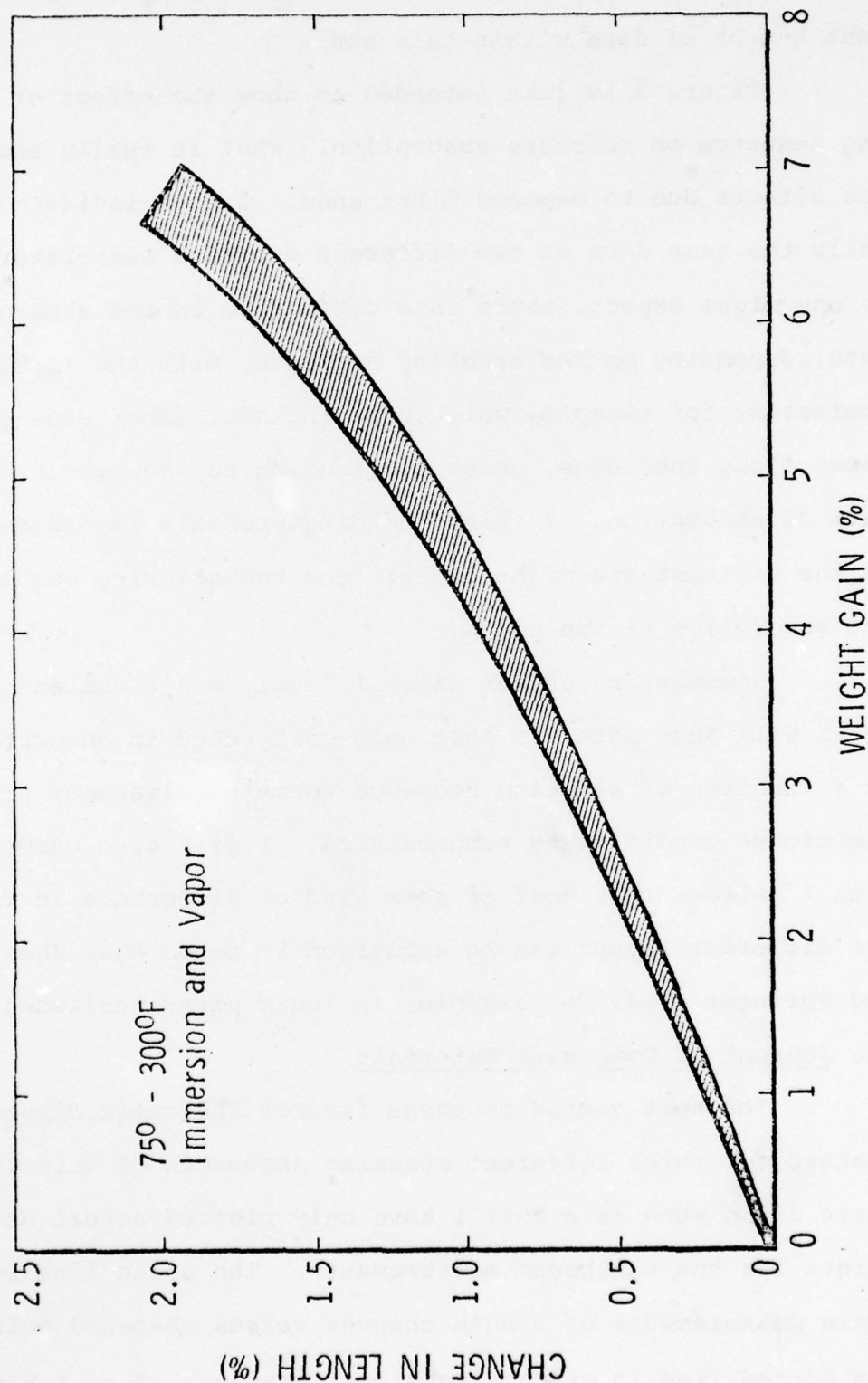
- 5208 RESIN CASTINGS
- (0) 8, 24
- (0/+45/0/-45)S, 3S
- (+45/0/-45/0)S, 3S
- (0/90)2S, 6S

* Not All Measurements at Each Condition

INCREMENTAL LENGTH CHANGE VS. MOISTURE ABSORPTION

5208 NEAT RESIN

FIG. 2



about something like 13,000 data points, so there are a significant number of data within this band.

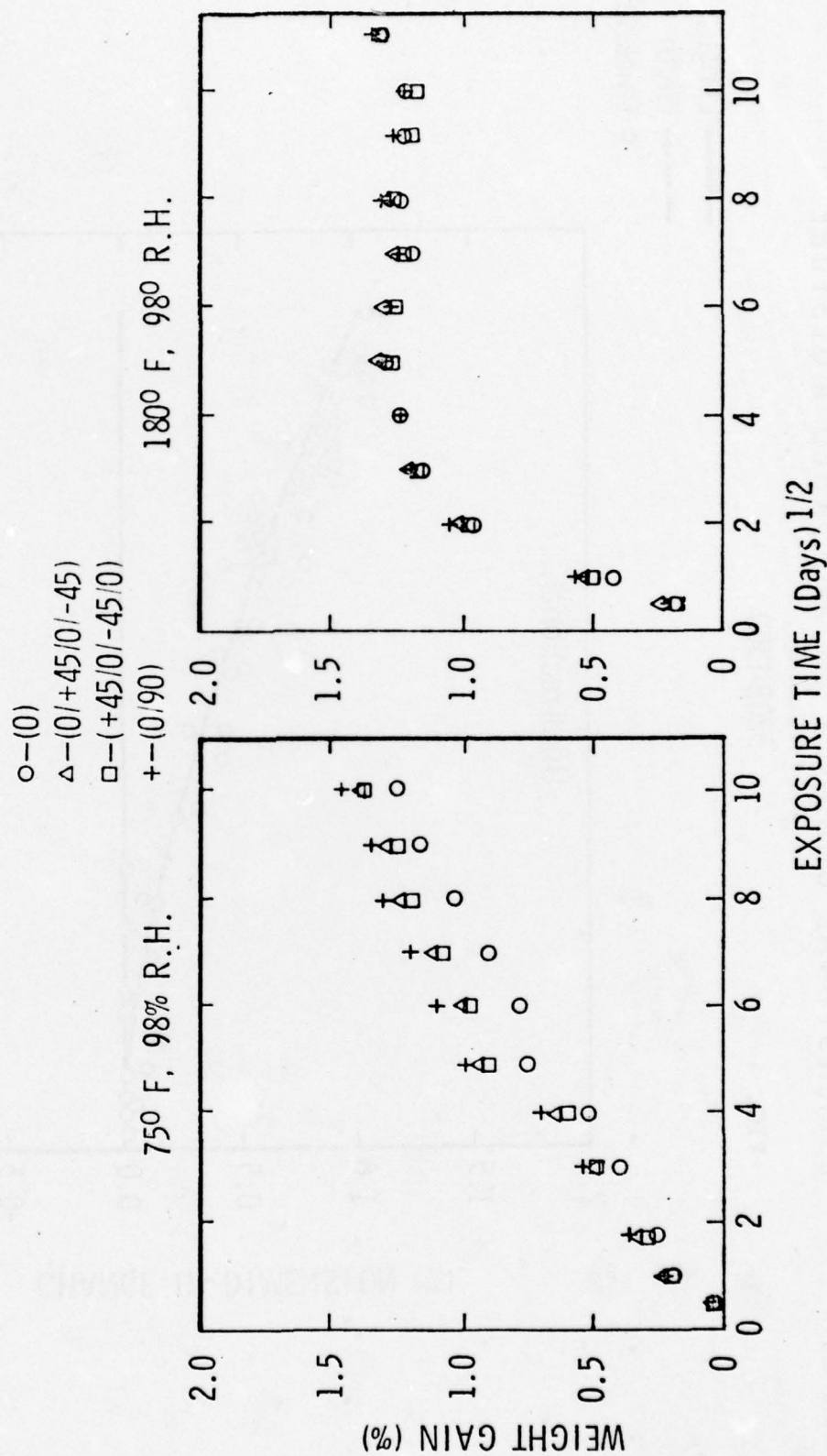
Figure 3 is just intended to show the effect of stacking sequence on moisture absorption. What it really shows is the effects due to exposed fiber ends. I have indicated basically the same data at two different exposure temperatures. As one might expect, there is a difference in the absorption rate, depending on the stacking sequence, with the (0/90) laminates, for example, which have the most fiber ends exposed along the edges, generally tending to show the highest rate of absorption. I think the data probably is ordered in the way that one might expect from the stacking sequence and absorption at the edges.

However, an effect which I really won't comment on, but I will just note, is that this difference in absorption as a function of stacking sequence seems to disappear at the higher conditioning temperatures. I will also comment that I believe that most of this kind of difference in rate for different layups can be explained in terms that Shen and Springer used, for example, in their paper published in the Journal of Composite Materials.

The next series of three figures indicates dimensional changes for three different stacking sequences of this laminate. There is so much data that I have only plotted actual data points for the thickness measurements. The solid line represents measurements of length changes versus absorbed moisture. The dotted line is width dimensional changes. Then I have

FIG. 3 MOISTURE ABSORPTION VS. STACKING SEQUENCE

5208/T300

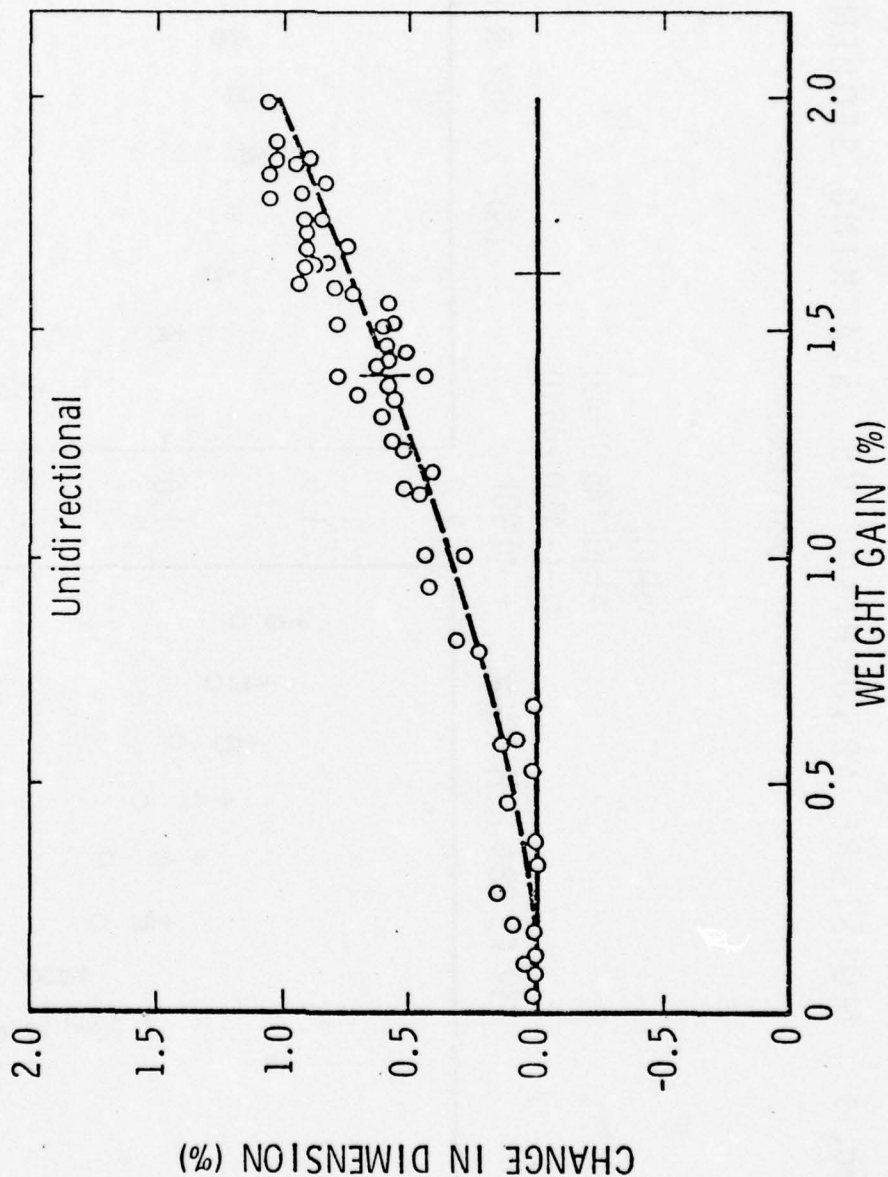


DIMENSIONAL CHANGES VS ABSORBED MOISTURE

5208/T300

FIG. 4

— Length
- - Width
o Thickness



overlaid the actual data for the thickness changes. The bars indicate the spread in the data for the length and the width, and as you see, for the unidirectional laminate, the width and thickness changes are very consistent.

Figure 5 shows results for $(0/+45/0/-45)_S$ laminates. Once again, in fiber controlled directions, namely length and width in this case, there is essentially no change in dimension versus absorbed moisture. The thickness changes look about the same in this case as for the unidirectional laminates.

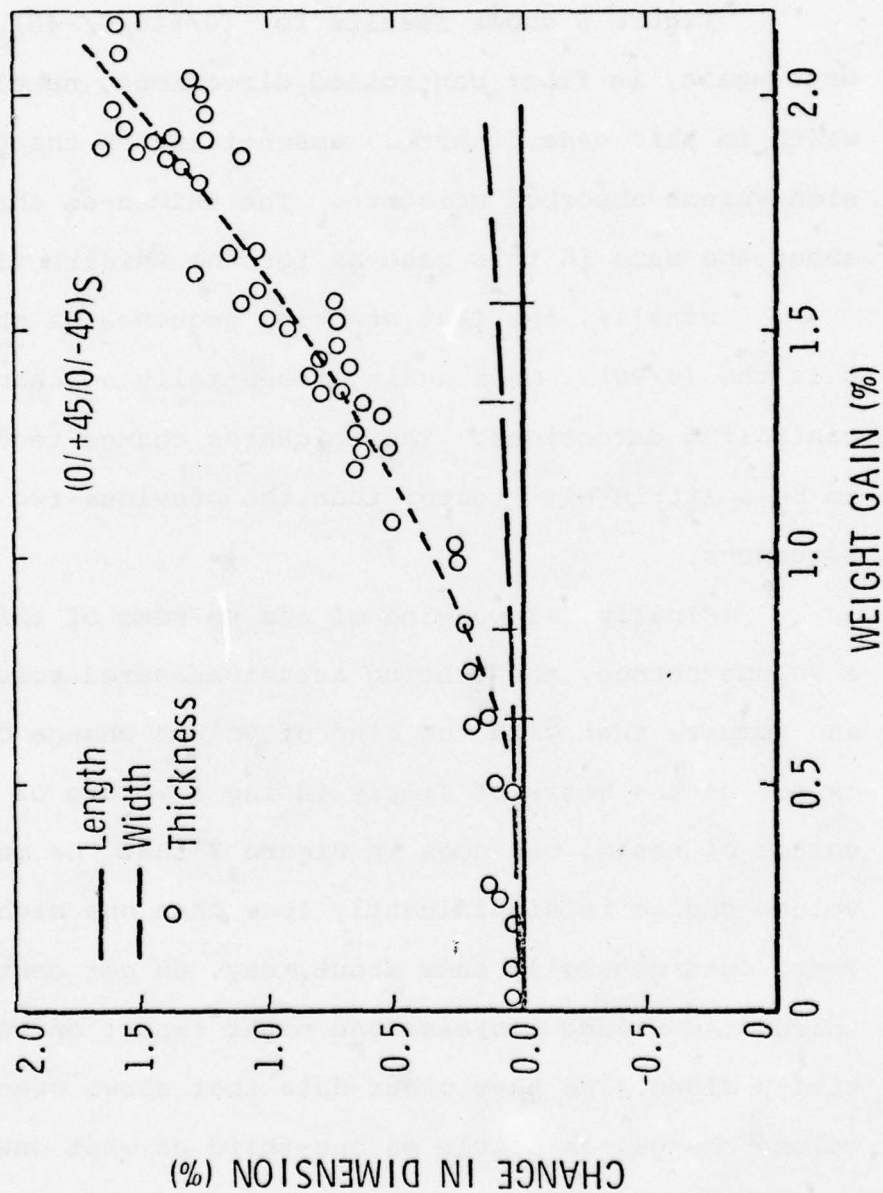
Finally, the last stacking sequence as shown in Figure 6 is the $(0/90)$. Once again, essentially no change in fiber controlled directions. The thickness change tends to appear to be a little bit greater than the previous two stacking sequences.

Finally, if we kind of add up some of this data into a volume change, these being actual measured volume changes, and compare that with the kind of volume change one might expect on the basis of simply adding a volume of water to a volume of resin, one sees in Figure 7 that the measured volume change is significantly less than one might expect. These data generally show about, say, 60 per cent to two-thirds the volume increase one might expect on volume additivity alone. We have other data that shows even a lesser volume change, as little as one-third of what one might expect, theoretically.

The next set of information I'd like to talk to you about is the work of Harris Carter and myself on fluid

DIMENSIONAL CHANGES VS. ABSORBED MOISTURE

FIG. 5 5208/T300

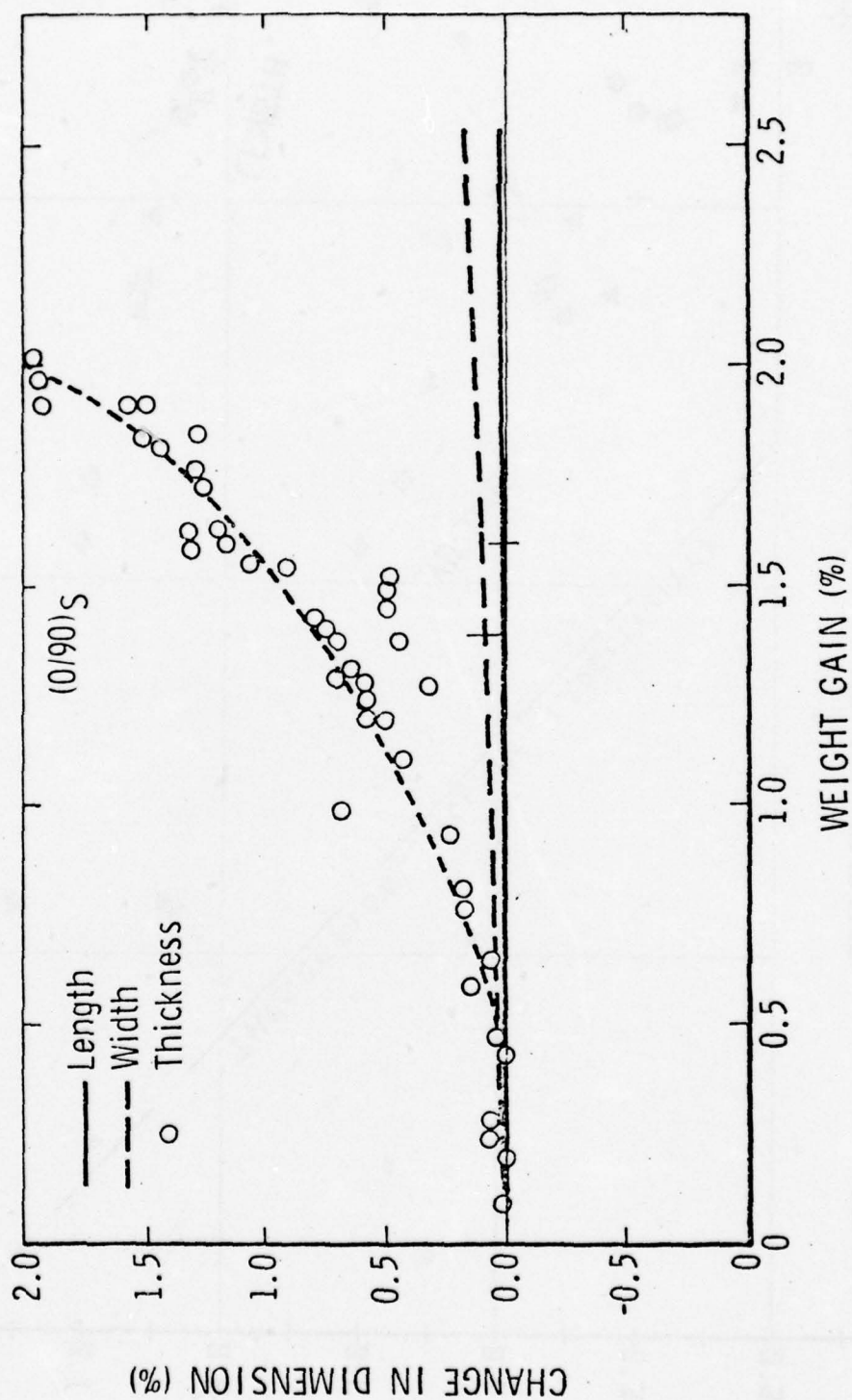


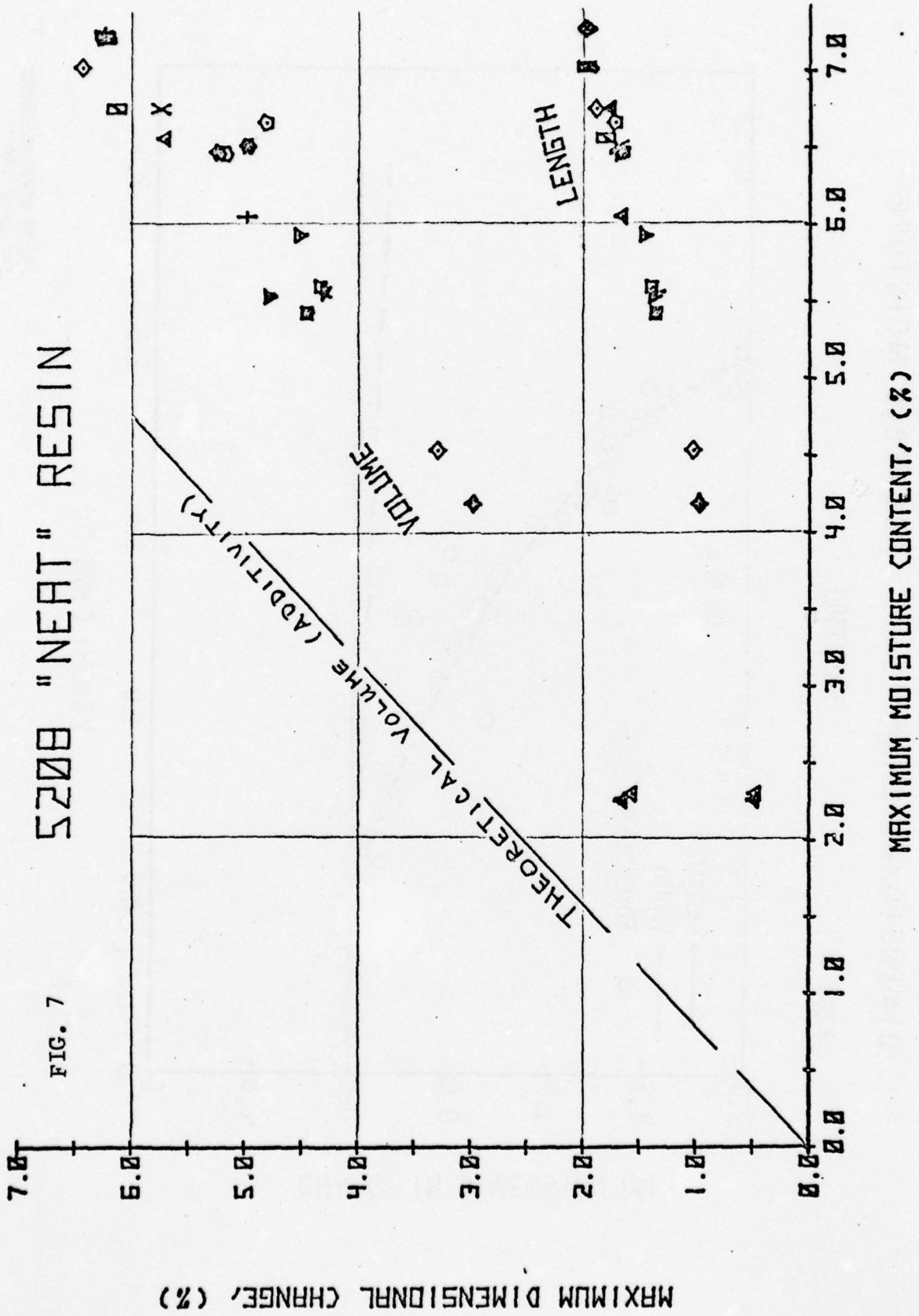
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DIMENSIONAL CHANGES VS. ABSORBED MOISTURE

FIG. 6

5208/T300





absorption in neat 5208 resin. In Figure 8 we plot absorption rate plotted in moles per unit surface area of the specimen for various liquids: water, methanol, ethanol, hexane, and carbon tetrachloride. These were chosen on the basis of having different capabilities for hydrogen bonding. If one looks at the initial stages of absorption in terms of moles per square inch versus square root of exposure time, one sees linear curves which correlate generally with the molecular weight of the absorbed species.

We have plotted these units on this graph so that if we plot the slopes of these curves on the next graph (Figure 9) as a susceptibility parameter, we find a reasonable correlation between that parameter, the molecular weight of the absorbed species, and its vapor pressure. The correlation we find is interesting, but we don't pretend to understand or even believe that it means anything. I will just say that if one looks at this quantity ϕ , which you see in generally equal to the saturation level in percent weight gain times the square root of the diffusion coefficient, we see that it correlates inversely with the molecular weight and inversely with the vapor pressure of the liquid.

Finally, in Figure 10 we have a similar kind of curve, namely, the initial susceptibility as a function of post-curing duration of the resin. Here we have plotted simply straight weight gain in milligrams, but this can be converted directly to this susceptibility parameter, and you see that as we go from no post-cure to the standard four hours at 400°F

FIG. 8 INITIAL MOLAR ABSORPTION OF VARIOUS PURE LIQUIDS
IN IMMERSSED 5208 NEAT RESIN (72°F)

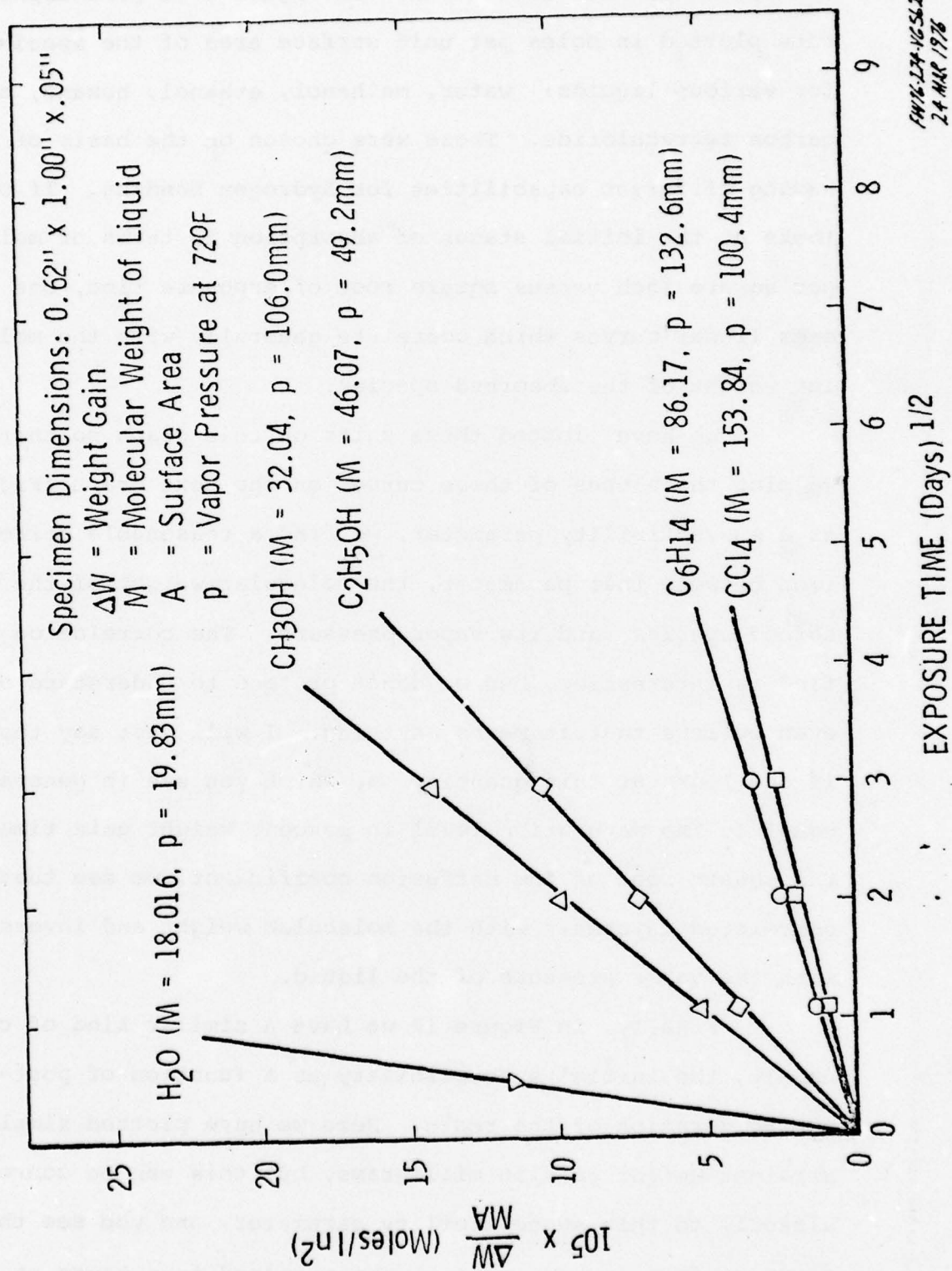
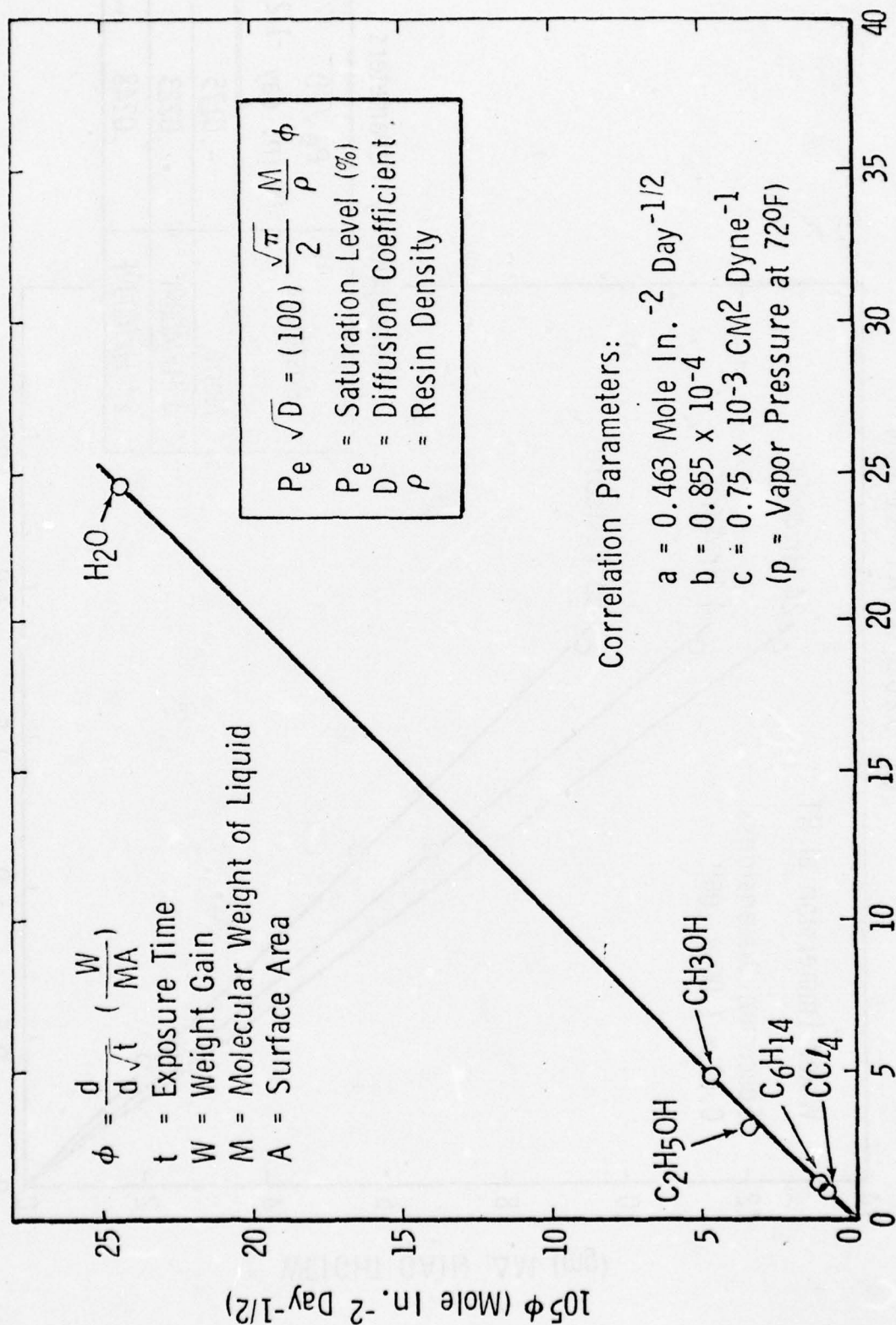


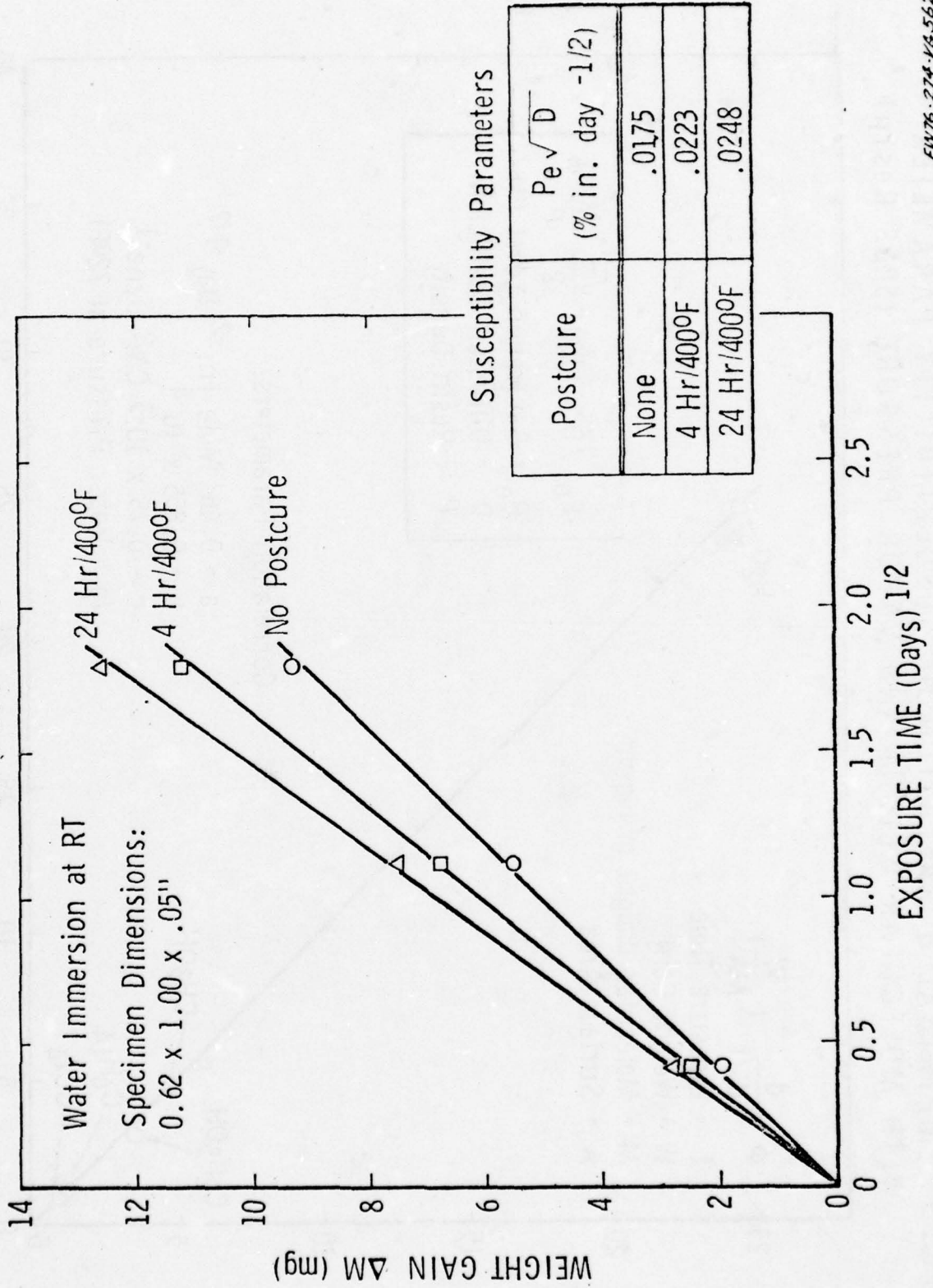
FIG. 9 EMPIRICAL CORRELATION OF SUSCEPTIBILITY PARAMETER
WITH MOLECULAR WEIGHT AND VAPOR PRESSURE (5208 Resin)



$10^5 a (M^{-9/4} + b)/\ln cp$

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FIG. 10 EFFECT OF POSTCURE ON MOISTURE SUSCEPTIBILITY
OF 5208 NEAT RESIN



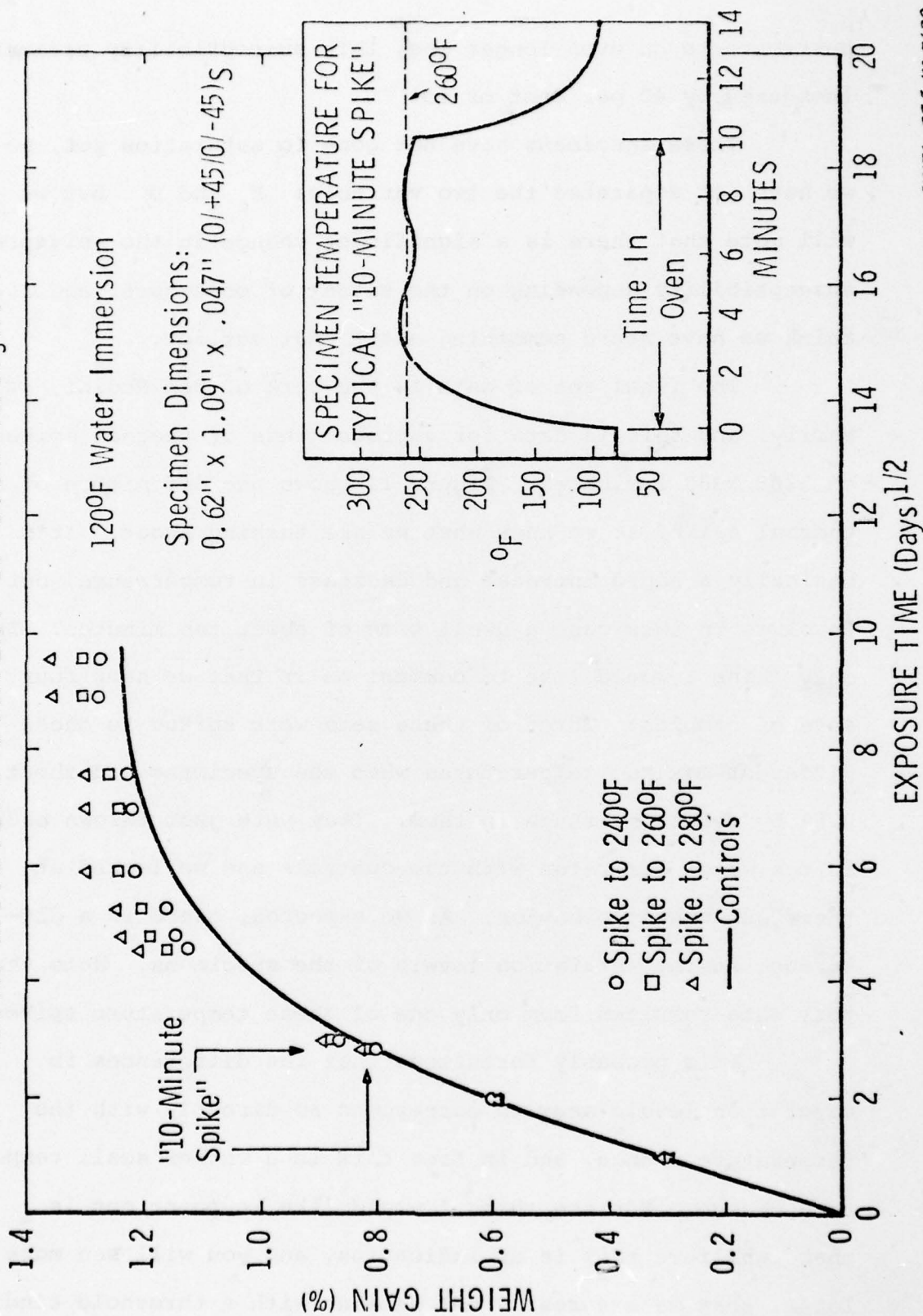
post-cure to an even longer one, this susceptibility parameter increases by 40 per cent or so.

These specimens have not gone to saturation yet, so we have not separated the two variables P_e and D but we will note that there is a significant change in the moisture susceptibility depending on the extent of post-cure, and I think we have heard something about that earlier.

The final set of data is the work of Ben Rodini, primarily, and this is data for various kinds of thermal spikes on 5208/T300 laminates. Figure 11 shows one definition of a thermal spike, so we know what we are talking about. It's basically a rapid increase and decrease in temperature, but involves in this case a dwell time of about ten minutes. The only thing I would like to comment on is that we have four sets of samples. Three of these sets were spiked to these different maximum temperatures when the specimens had about 0.8% by weight moisture in them. They were just thrown back in the water immersion with the controls and we looked at their subsequent behavior. As we expected, there is a difference in the saturation levels of the specimens. Note that this data resulted from only one of these temperature spikes.

It's probably fortuitous that the differences in saturation levels seem to correspond so directly with the temperature change, and in fact this is a rather small temperature change. But the thing I would like to point out is that I believe this is an indication, and you will see more later, that we are really not dealing with a threshold kind

FIG. 11 EFFECT OF "10-MINUTE SPIKE" ON 5208/T300
WITH MOISTURE CONTENT OF 0.8% (Weight)



of effect. I think we are dealing with a continuous effect that only varies in degree, depending on our exposure conditions.

Figure 12 shows the same kind of data, but the spike is done here at two different moisture contents, one in which the samples had about half per cent moisture by weight and the others about .8 per cent. In the previous case we saw a kind of monotonic dependence on temperature and here we see sort of a monotonic dependence on moisture content.

Well, this isn't really the way to look at spike effects and so in the final two figures I would like to show you more recent data.

In this case we have immersed some specimens, once again these are unidirectional 8-ply laminates, until all the specimens contained about .6 per cent moisture by weight. We then subjected several sets of the specimens to the kind of fast temperature spike shown in Figure 13: fast, no dwell time at temperature, one spike. After the spike all the specimens were desorbed completely to essentially their original weight, and then this Figure is a plot of their reabsorption. Once again we have plotted a quantity, weight gain times thickness times a constant, which translates directly into the susceptibility parameter.

Now, I won't claim that there is any spike effect going from the controls to a 200 degree spike, because the statistics just aren't that good. But you do see there is an irreversible change, even at as low as 250 degrees Fahrenheit,

FIG. 12 EFFECT OF "10-MINUTE SPIKE" ON 5208/T300 WITH DIFFERENT MOISTURE CONTENTS

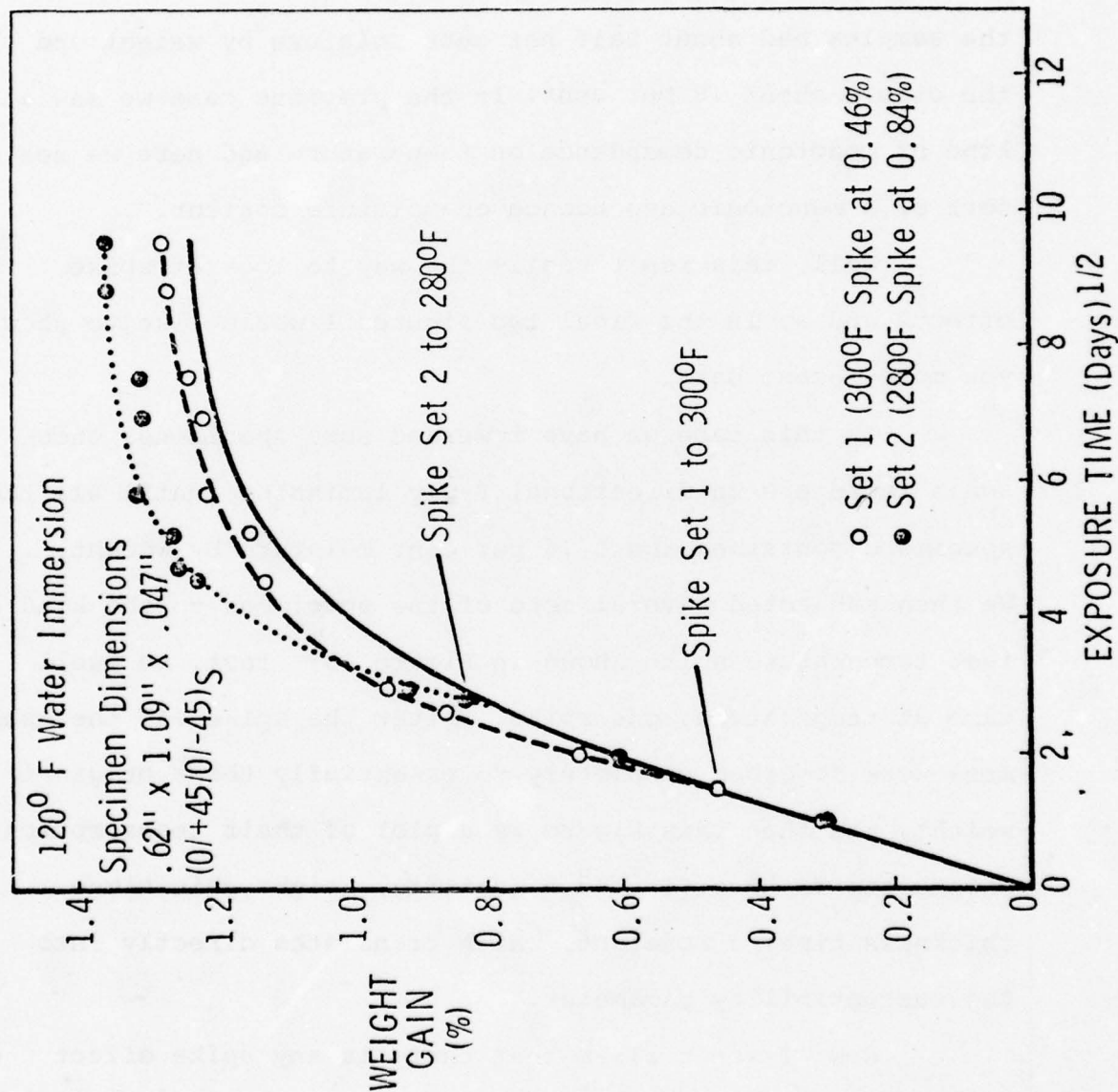
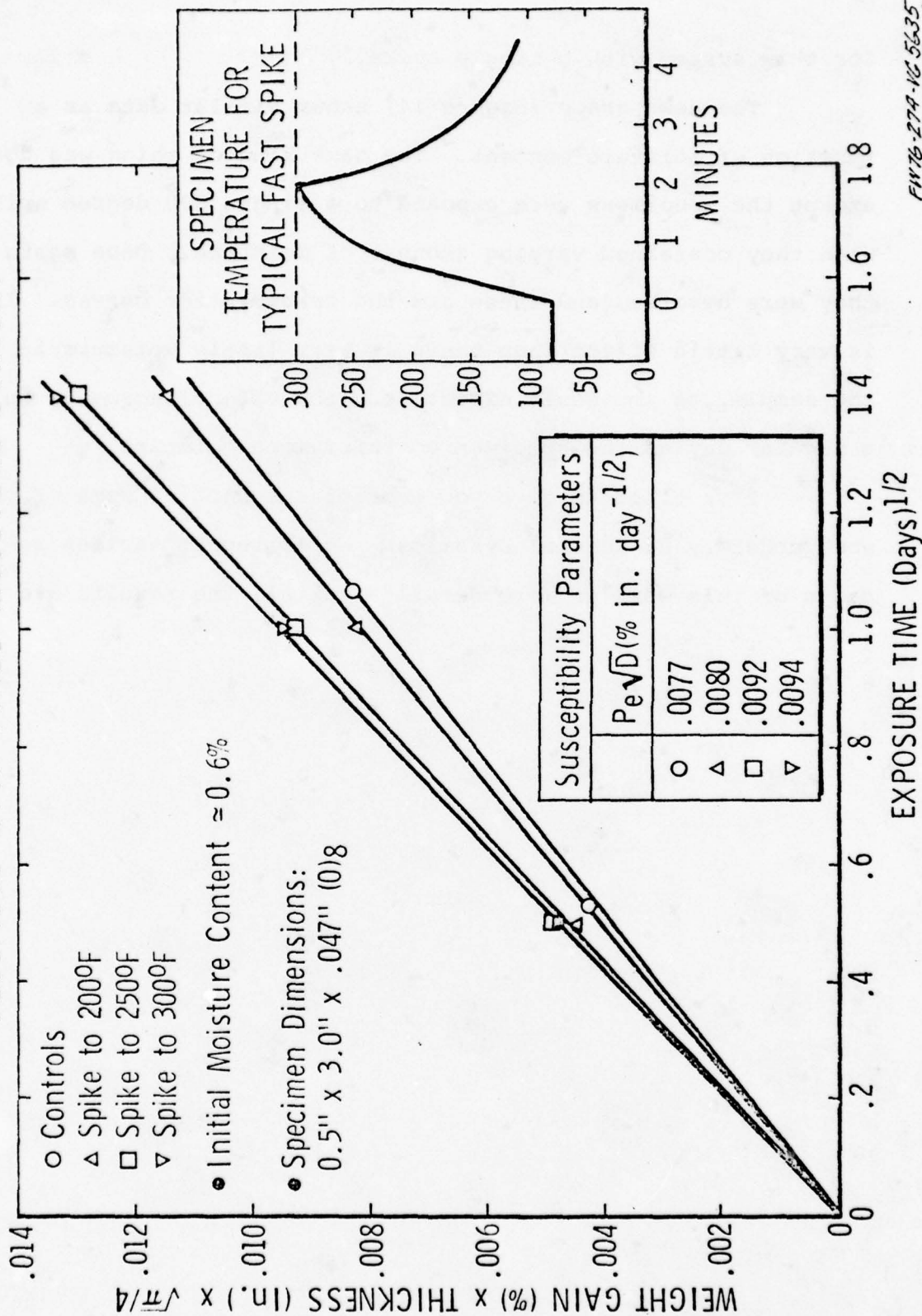


FIG. 13 EFFECT OF FAST SPIKES TO DIFFERENT TEMPERATURES ON
5208/T300 WITH FIXED MOISTURE CONTENT

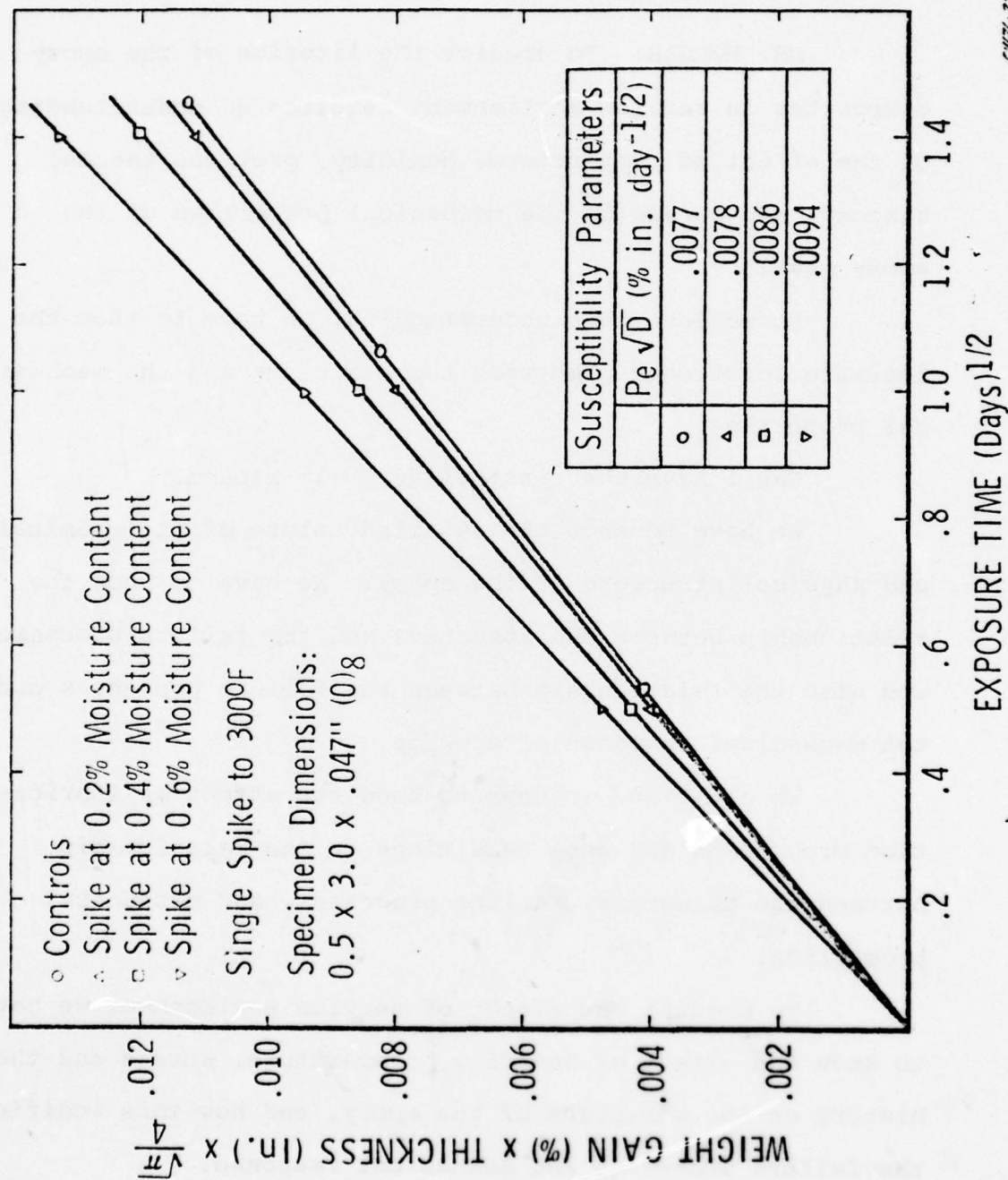


for this system with a single spike.

The next graph (Figure 14) shows similar data as a function of moisture content. The same kind of thing was done except the specimens were exposed to a single 300 degree spike when they contained varying amounts of moisture. Once again they were desorbed and these are the reabsorption curves. There is very little effect when there is very little moisture in the sample, as you would expect, but the effect increases in a regular way as the specimen contains more moisture.

I've tried to give you a brief snapshot of some of the work underway at General Dynamics. We'll report various aspects of this work in more detail after all the results are in.

FIG. 14 EFFECT OF 300°F FAST SPIKE ON 5208/T300
WITH DIFFERENT MOISTURE CONTENTS



DR. MC CULLOUGH: Thank you very much.

Our next speaker is R.J. Morgan, from McDonnell-Douglas.

DR. MORGAN: To predict the lifetime of the epoxy composites in service environment requires an understanding of the effect of temperature, humidity, previous thermal history, and stress on the mechanical properties of the epoxy itself.

To achieve this understanding, we have to know the intimate relationship between the structure and the mechanical properties.

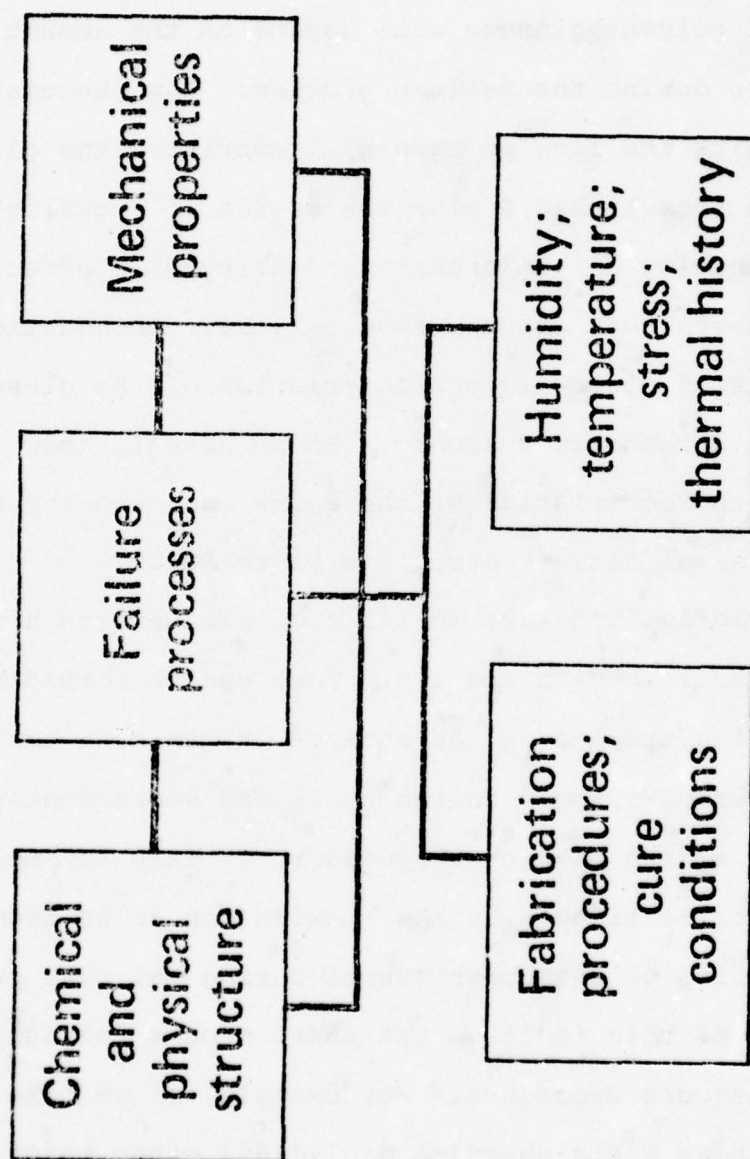
Can I have the first slide, (M-1) please?

We have to know the detailed nature of the chemical and physical structure of the epoxy. We have to know the relationship between the structure and the failure processes, and also the relationship between the failure processes and the mechanical response of epoxies.

In addition, we have to know the effect of fabrication procedures and cure conditions on the relationship between the structure, failure processes, and mechanical properties.

To predict the effect of service environment we have to know the effect of humidity, temperature, stress and thermal history on the structure of the epoxy, and how this modifies the failure processes and mechanical response.

In this presentation, we will discuss the structure-



property relations of epoxies and how these observations relate to the effect of relative humidity and elevated temperatures on epoxies themselves. The primary structural parameters affecting the failure processes and mechanical properties of polymer glasses will depend on the amount of flow that occurs during the failure process. Any phenomenon that inhibits the flow process will embrittle the glass.

In crosslinked resins the degree of crosslinking and the distribution of the crosslink density will affect the flow processes that occur during failure. In addition, the stress-raising microvoid characteristics of the glass will affect the mechanical response. So we have to know the microvoid characteristics of the epoxy and also the details of the physical network structure of the epoxy.

Briefly, I'd like to first of all mention how microvoids can be formed in epoxies. They can be formed by air bubbles being trapped in the epoxy. We can have low molecular weight material trapped in the glass and subsequently eliminated during the post-cure procedures. This low molecular weight material trapped in the epoxies can arise from inhomogeneous mixing of the constituents during the cure procedure. An example of this is if we get phase separation during some part of the cure procedure. For example, if we take an ideal system such as a bis-phenyl-A diglycidyl ether based epoxy in which the unreacted epoxy monomer contains crystals of pure monomers. (The pure monomer crystallizes as square platelets of ten microns in size.) When we partially cure at room

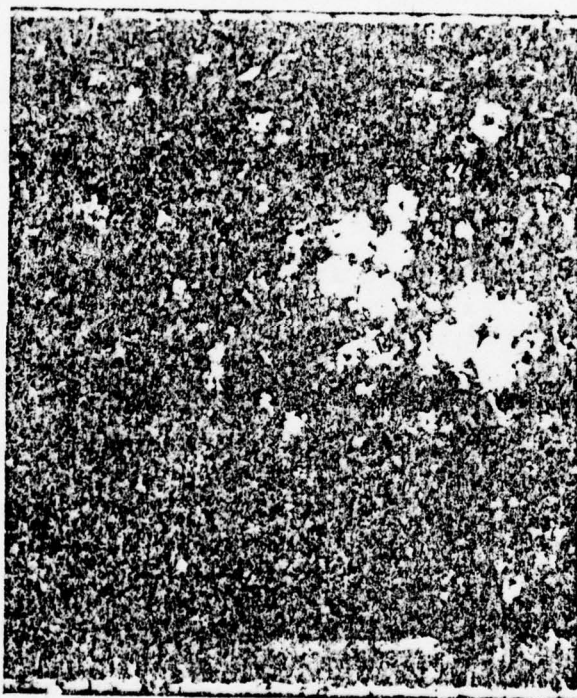
temperature the crystals will remain imbedded in the partially cured glass. These crystals have a melting point of 42 degrees Centigrade.

Now, if we post-cure above 42°C, in the 70-180°C range, the crystals will melt and we will have islands of liquid monomer which will subsequently be eliminated from the glass and produce microvoids and associated stresses because of volatilization of the low molecular weight material, as shown in the next slide. (M-2)

We show light scattering patterns produced by such an epoxy system and the light scattering patterns we believe are due both to the microvoids and the stresses surrounding the microvoids which result from volatilization of the low molecular weight material.

For this epoxy system the microvoid production can easily be avoided by just melting the crystals prior to curing the system. However, in some of the latest epoxy systems little data is available on any phase separation during the cure procedures. Little is known on how low molecular weight material is trapped in the glass and can subsequently be eliminated during the cure procedures.

We'd now like to turn to the network structure of epoxies. The crosslinked network formation of epoxies is a diffusion controlled process and will depend on the functionality of the particular epoxy system. Generally, to overcome the mobility restrictions of the glassy state such that every group reacts we usually have to go to temperatures where we

400 μm

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start to get thermal degradation via chain scission or additional crosslinking. If you look at the infrared spectrum you will see extremely complex infrared spectra if we go to the conditions where every group will start to react. In addition, the material will start changing color due to the formation of stable free radicals. The overall crosslink density of epoxies is generally monitored by infrared analysis, dynamic mechanical measurements, swelling measurements, differential scanning calorimetry measurements, thermal conductivity and/or dielectric loss measurements.

We believe the crosslink density distribution plays a key role in the failure processes and mechanical response of epoxies. Highly crosslinked regions, sixty angstroms to 10 microns in size, have been reported by many workers in crosslinked resins. The conditions for the formation of a heterogeneous rather than a homogeneous system will depend on polymerization conditions such as temperature, solvent and/or chemical composition.

These regions have been described as agglomerates of colloidal particles or floccules in a low molecular weight interstitial fluid.

Solomon and co-workers have suggested that a two-phase system is produced by microgelation prior to the formation of a macrogel.

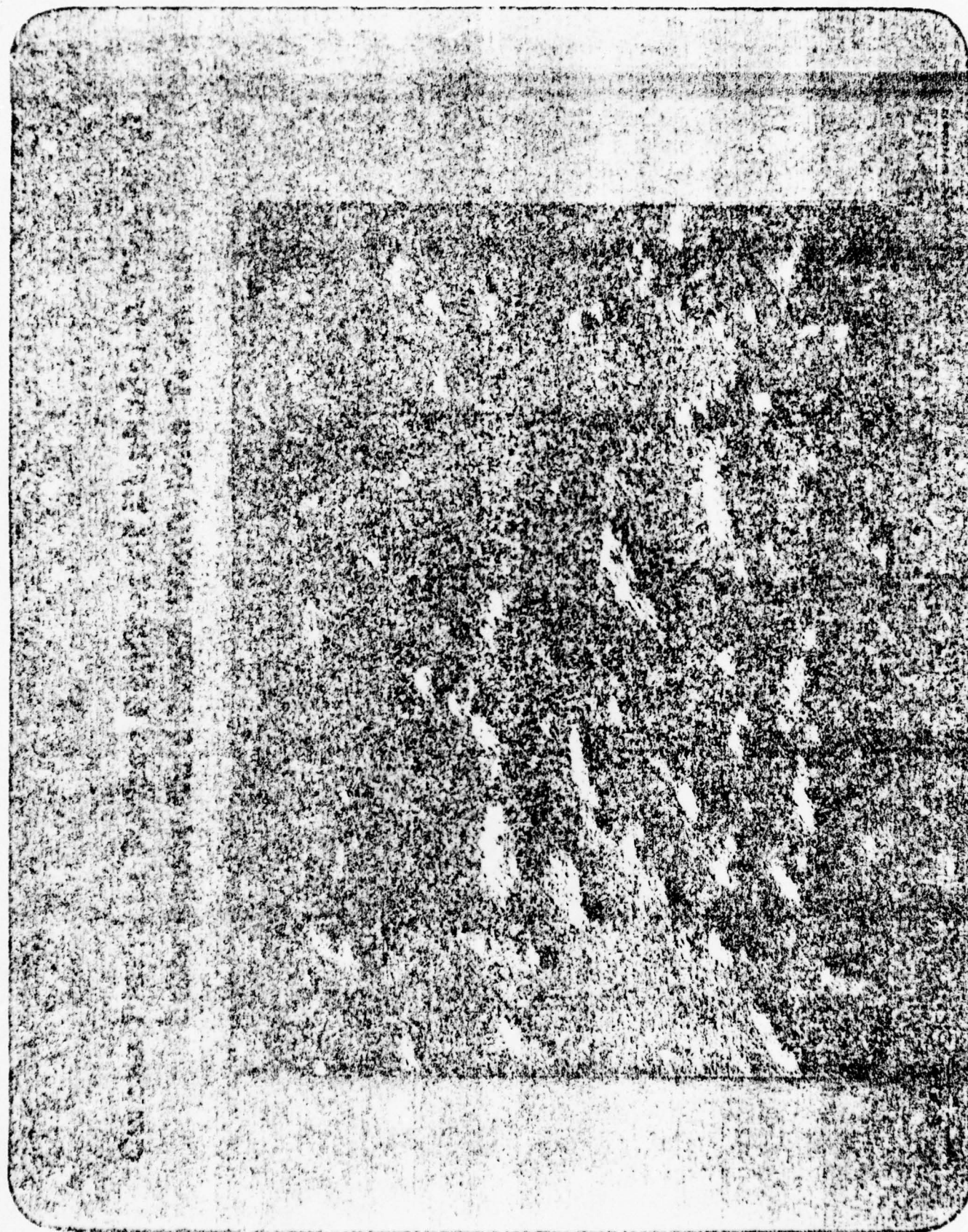
Kenyon and Nielsen have suggested that the highly crosslinked microgel regions are loosely connected during the later stages of the curing process. These regions have

been reported to be only weakly attracted to the surrounding matrix and their size varies with cure conditions, proximity of surfaces and the presence of solvents.

These regions can be observed by electron microscopy. We can leach the surface of epoxies with organic solvents which will in many epoxies dissolve the low molecular weight soluble material and leave regions of high crosslink density exposed on the surface as shown in the next slide. (M-3)

We see regions of 200 to 500 angstroms in size protruding above the surface. We generally learn more if we look at thin epoxy films by bright-field transmission electron microscopy, particularly if we strain the film directly in the electron microscope and see how it deforms.

This next slide (M-4) is a bright-field transmission electron micrograph. The dark regions indicate thicker areas or more highly ordered regions. This film was originally of uniform density distribution. We have strained this film fairly fast in the electron microscope and we can see it breaks up inhomogeneously, indicating there are regions which preferentially flow in this epoxy system. Other evidence that many epoxies are heterogeneous in nature comes from fracture topography studies. For example, if we introduce excess epoxy monomer into an epoxy system which is cured by an amine and we cure at room-temperature, the excess epoxy will recrystallize between the microgel regions. If we then heat the sample and drive off the excess epoxy monomer and fracture the specimen we see a heterogeneous fracture surface,



M-3

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20 μ m

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as shown in the next slide.(M-5)

You see microcracking and you see inhomogeneous regions across the whole fracture surface.

The relationship between the network structure, microvoid characteristics, the failure processes and mechanical response has received little attention. Localized plastic flow has been reported to occur during the failure processes of epoxies that are prepared from the stoichiometric mixture and supposed to be completely crosslinked; yet they flow. Furthermore, in a number of cases the fracture energies associated with epoxy failures are anywhere from 100 to 1,000 times greater than that theoretically expected for brittle fracture.

The epoxy systems we have looked at (we have been concentrating on, bis-phenyl-A, diglycidyl ether systems) fail by a crazing process.

We have strained films directly in the electron microscope, as shown in the next slide.(M-6) This is a thick film which is approximately about a micron thick. We have lightened the micrograph to show this large fibrillar structure. This fibril is shown in more detail in the next slide (M-7) and it is evident it is heterogeneous.

Indeed, in this fibril we can actually see what appears to be a strained crosslinked network structure.

Can I have the next slide,(M-8) please.

Again, we can see in this other part of the fibril that it's breaking up inhomogeneously and we have preferential regions of flow. It appears the constituent particles are

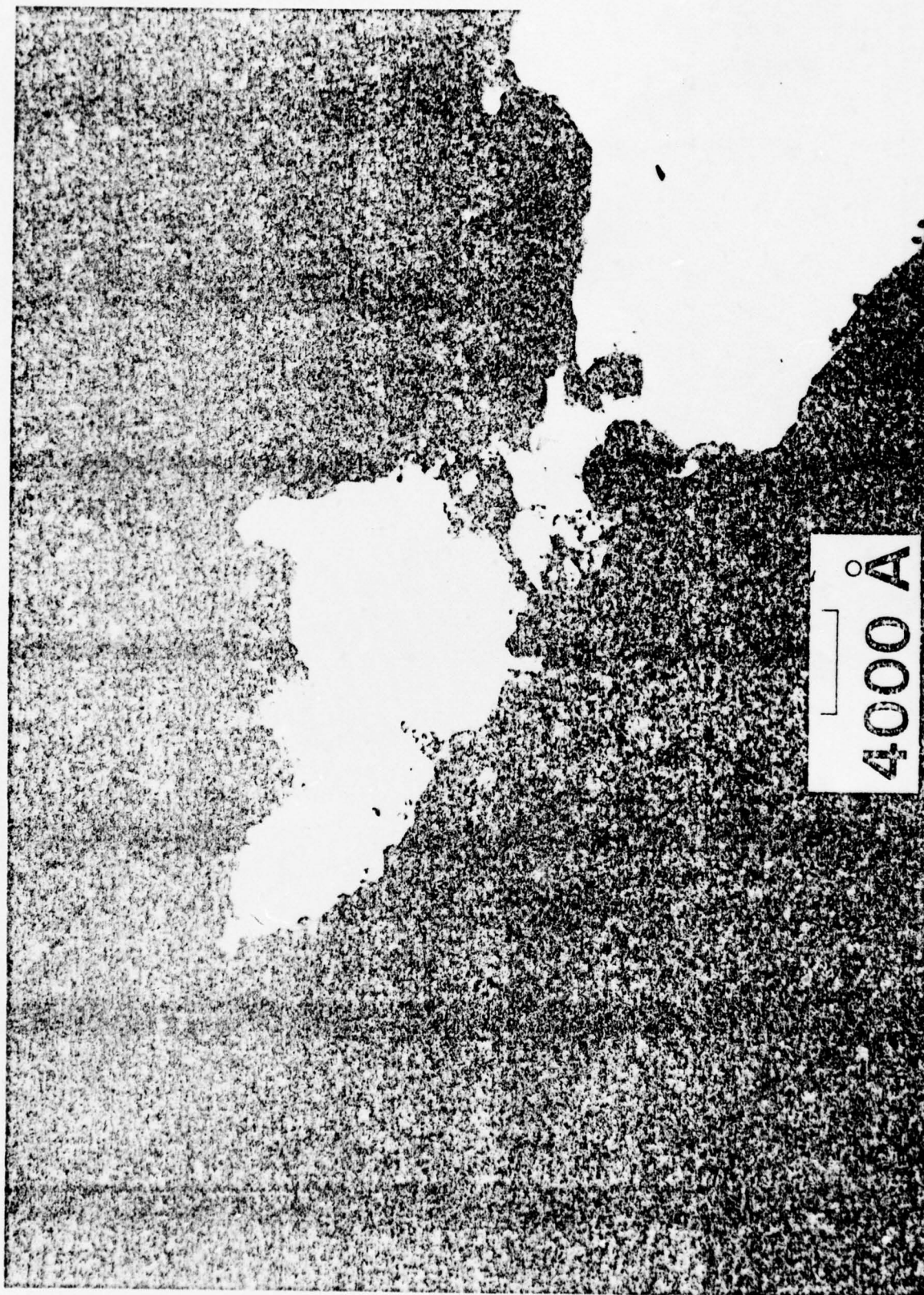


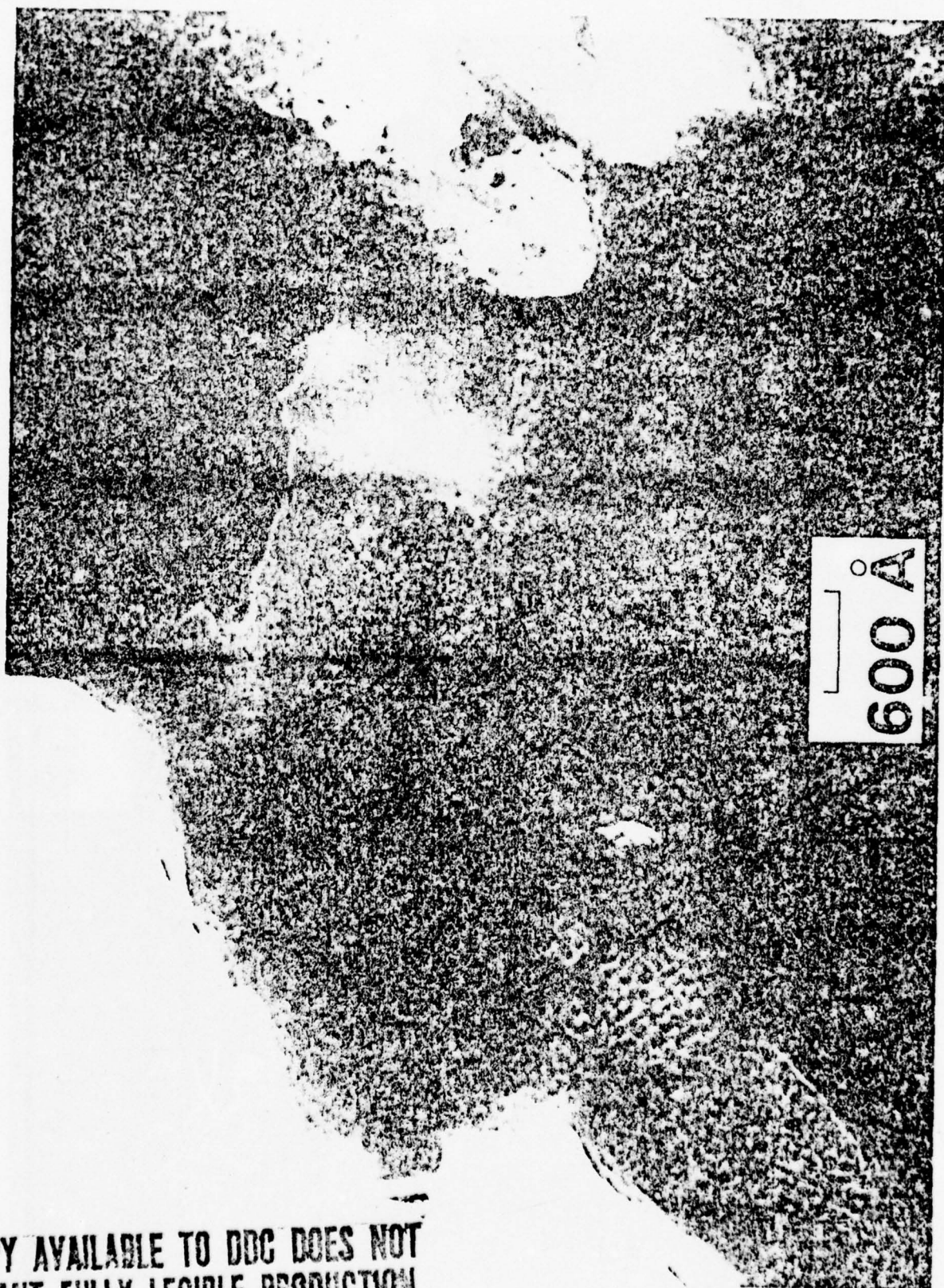
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M-5

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4000 Å

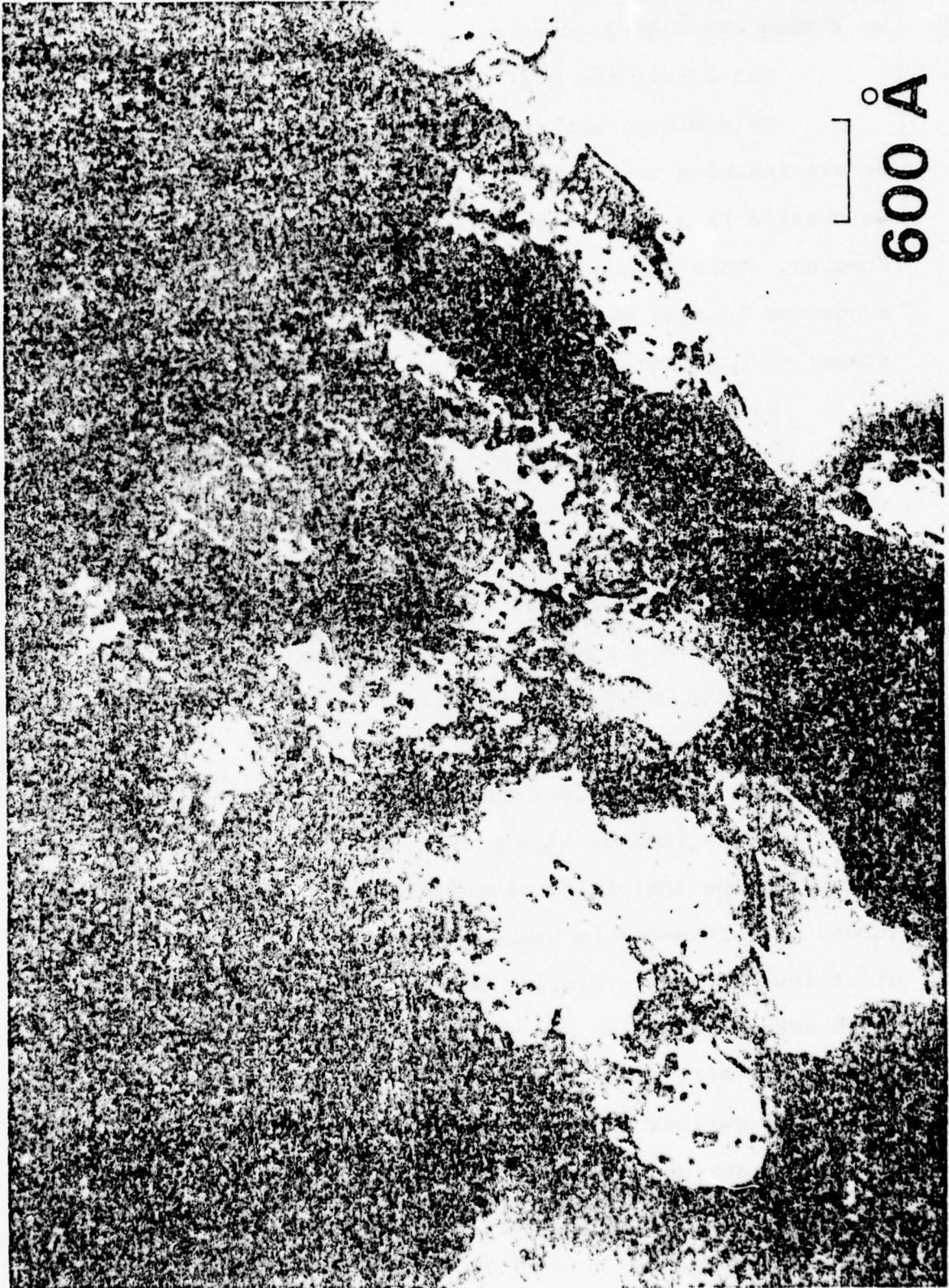




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225



about 80 angstroms in size and these particles do not break up during the flow processes.

Can I have the next slide, (M-9) please.

This micrograph is a blowup - I apologize for this - we are reaching the limits of the electron microscope. What we observe is a network of interconnected macromolecular domains. This is consistent with what Kenyon and Nielsen suggested in that microgel regions form during the initial stages of cure and then they later interconnect together.

May I have the next slide, (M-10) please.

Looking at thinner epoxy films, this is about a thousand angstroms thick, we see a crude craze here. These regions are of high crosslink density and we see there are fibrils forming across here, and it is evident the drawing of new material into the crazed fibril will be inhibited by such regions of high crosslinked density at the craze-matrix boundary interface.

It is evident from these studies that the inextensibility of regions of high crosslink density within a crazed fibril and the inhibition of the drawing of new material across the craze-matrix boundary interface, due to presence of regions of high crosslink density at the interface, will cause strain hardening and possible fracture of the fibrils and, hence, will enhance crack propagation.

If we look at the fracture topography of epoxies in the slow crack-growth initiation region - the next slide (M-11) please - we see a terraced type structure. We believe this is

750 Å



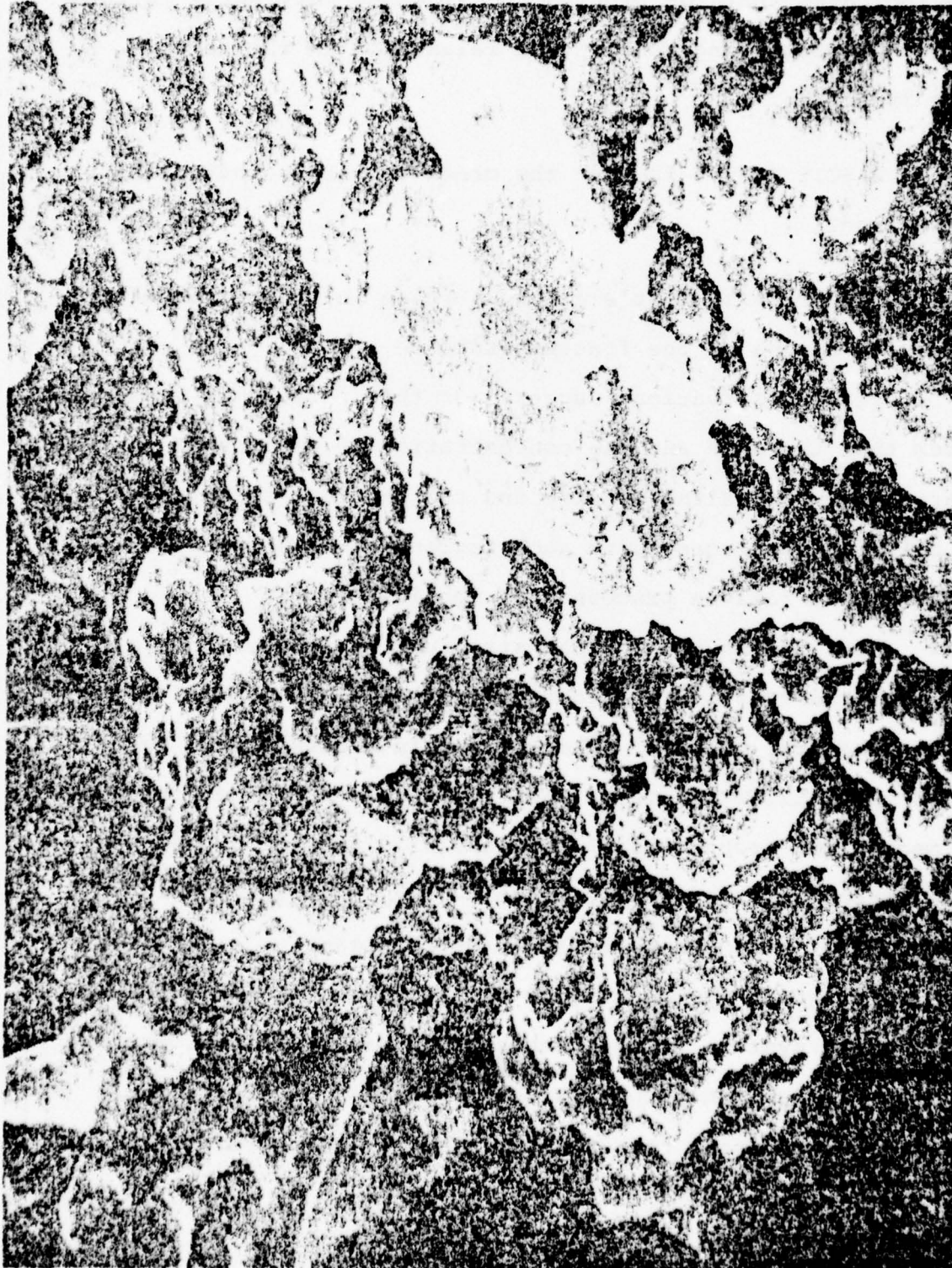
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6.6 μ m

due to the fact that the cavity within the craze is growing simultaneously with the craze and the crack propagates through a poorly developed craze which consists of coarse fibrils. This indicates that the fibrils are breaking very early in the game. We are getting very little relaxation in the network after fracture.

A SCIENTIST: Is that the crack tip or is that along the surface?

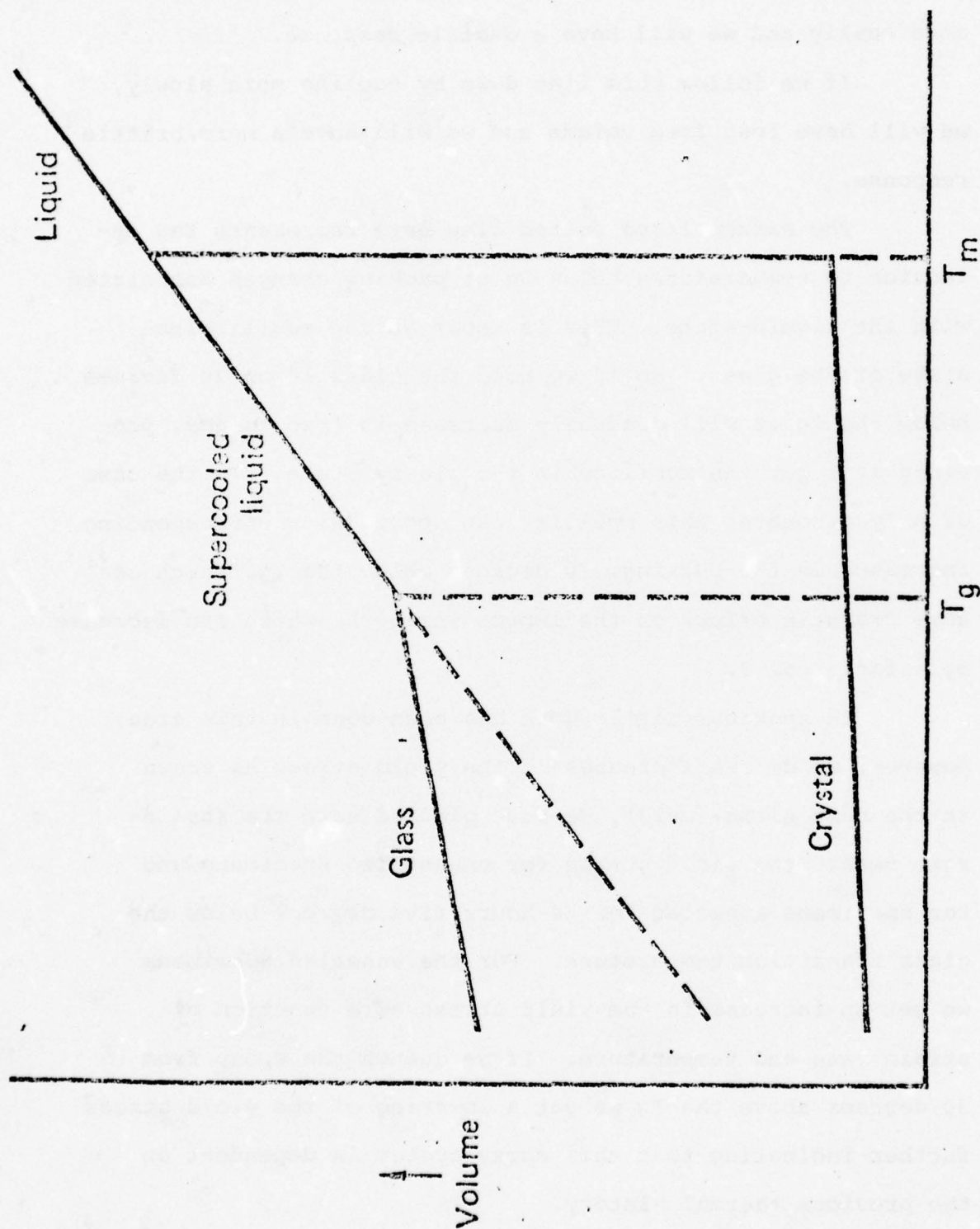
DR. MORGAN: That's at the surface in the center of the mirror region of the fracture surface.

These observations suggest for this particular epoxy system that the size and the concentration of regions of apparent high crosslink density and the physical structure of the material interconnecting such regions control the flow processes and failure processes of epoxies.

Now, the major physical structural parameter controlling the flow processes in the lightly crosslinked regions of epoxies will be the free volume. (That volume in excess of the best-packed crystalline volume.) The free volume and, therefore, the mechanical properties of epoxies, will depend on the previous thermal history above and below the T_g of the epoxies.

May I have the next slide, (M-12) please.

We show a typical volume-temperature plot for a liquid-glass system. If we quench the glass rapidly from above the glass transition temperature, we will follow line like this and down to room temperature. We will, therefore, produce

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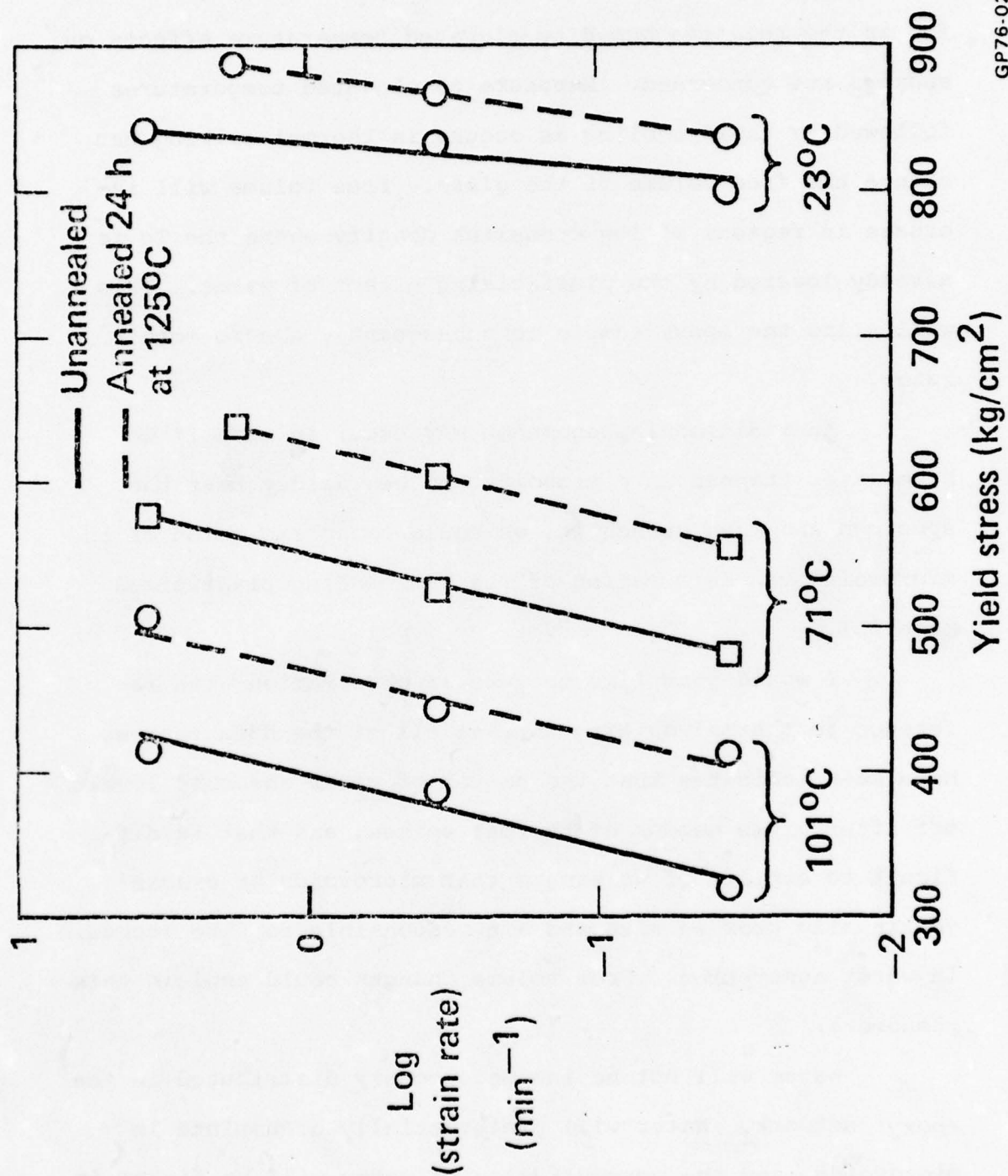
a large free volume, this will enable flow to take place more easily and we will have a ductile response.

If we follow this line down by cooling more slowly, we will have less free volume and we will have a more brittle response.

The extrapolated dotted line here represents the extension to temperatures below T_g of packing changes associated with the liquid-state. This is known as the equilibrium-state of the glass. So if we hold the glass 10 or 20 degrees below the T_g it will gradually decrease in free volume, provided it's got the mobility in the glassy state. In the case of polycarbonate, this mobility can occur, with corresponding increases in the packing, 70 degrees below the T_g , which can have dramatic effect on the impact strength, which can decrease by a factor of 8.

In epoxies, little work has been done in this area; however, we do see increases in the yield stress as shown in the next slide. (M-13) We have plotted here the strain-rate versus the yield stress for unannealed specimens and for specimens annealed for 24 hours five degrees below the glass transition temperature. For the annealed specimens we get an increase in the yield stress as a function of strain rate and temperature. If we quench the epoxy from 30 degrees above the T_g we get a lowering of the yield stress further indicating that this epoxy system is dependent on the previous thermal history.

A SCIENTIST: Tensile yield stress?



DR. MORGAN: Yes.

These observations have a number of implications as far as the relative humidity-elevated temperature effects on epoxies are concerned. Exposure to elevated temperatures followed by rapid cooling as occurs in thermal spiking can change the free volume of the glass. Free volume will increase in regions of low crosslink density where the T_g is already lowered by the plasticizing effect of water. This will allow the epoxy sample to subsequently absorb more water.

An additional phenomenon may occur in that if we have water trapped in microvoids and we rapidly heat the specimen and then quench it, we could cause expansion of the microvoids via deformation of the surrounding plasticized material.

I would just like to make an observation with reference to thermal spiking in that all of the data that we have seen indicates that the amount of water absorbed levels off after given number of thermal spikes, and that is difficult to explain if we assume that microvoids or cracks continually grow in size and are responsible for the increase in water absorption. Free volume changes could explain this phenomena.

Water will not be inhomogeneously distributed in the epoxy network. Water will preferentially accumulate in microvoids, and the concentration of water will be higher in regions of low crosslink density.

Now, it is these very regions which preferentially undergo flow during deformation. Hence, the plasticizing effect of water may be greater than that expected for a homogeneous distribution of water throughout the glass.

For an epoxy system which has been exposed to a stress, and a craze has started to propagate, water will accumulate in the porous craze structure over a period of time. This water can modify the craze-crack propagation as indicated in the numerous studies on effects of solvents on craze growth in many of other polymers. Water at the craze tip can have two opposing effects; first of all, it will soften the network at the craze tip, which should enhance cavitation which could be described as a solvent-crazing effect. However, we also have swelling of the network at the craze tip which will decrease the dilatational stresses and, therefore, decrease the cavitation.

The crazed fibrils themselves will be softened by the water, which will decrease their load-bearing capability.

There has been some recent evidence in the literature on solvent-induced crazing in polystyrene which suggests the distribution of the solvent or the water in the craze affects the failure mechanism. If the water diffuses to the outer fibrils first, which will soften them, the inner fibrils nearer the craze tip will carry a greater percentage of the load and, therefore, will fracture prior to the outer ones and we will get crack growth preferentially in the interior of the craze.

It is also possible that enhanced molecular mobility caused by water could allow some unreacted groups to form additional crosslinks. May I have the next slide, (M-1) please.

In conclusion, we would like to reiterate that to understand or predict the effect of humidity and high temperature on epoxy composites we have to know the structure property relationships of the epoxy itself. We have to know the detailed structure, how it's related to the failure processes and the mechanical response, and what are the effects of fabrication and cure procedures. Only then can we understand the exact effects of humidity, temperature, stress, and thermal history on the mechanical response of the epoxies.

Thank you.

DR. MC CULLOUGH: Thank you. The next speaker is Dr. P.H. Francis of the Southwest Research Institute.

2. Characterizations of Constitutive Properties

DR. FRANCIS: I need all the help I can get from this microphone because I am trying to combat a case of laryngitis, and only today have I begun to be able to speak again.

Usually, when I get up to talk before a technical audience on a technical subject it's about something in which I have been involved from a research point of view for some time. But today, however, is different. I have not done any first-hand research at all in the moisture effects on epoxy resin composites. Now, I say this not as a disclaimer for

anything I might say, but rather to tell you that my perspective on this problem is more of a mechanics man who looks at research developments in this particular area as an observer and not as a participant.

Perhaps then whatever I might lack in completeness may be compensated for in objectivity. Incidentally, since I have written this talk I have prepared a very brief bibliography, which just covers the points that I will address, and I am going to leave some copies here for any of you who might like to pick one up sometime. It's limited just to the scope of my particular presentation today. (See page 238)

Now, during this Workshop a number of presentations will bring out the phenomenological basis of the moisture absorption problem in epoxy composites. I am going to attempt not to overlap these presentations but rather to give you a brief appraisal as to where we are or where we might be from a mechanics standpoint in this general problem area.

As I see it, there are two broad issues involved. The first is to predict the time-dependent moisture content in a laminate under general environmental conditions. The second issue, then, is to predict property degradation and failure as influenced by moisture.

Now, of these two broad issues I am going to address only the first this afternoon because I feel that without a good understanding of the mechanics of moisture absorption there is scant hope for any progress to be made in developing a model for failure or mechanical property degradation. I

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am going first to give you - and this will be somewhat redundant with what Ted Reinhart and others have given today - somewhat of a very brief experimental background. And the main thrust of what I am going to talk about first will deal with a mechanical description of moisture absorption.

I am going to show you just a very few slides. I am not going to show you any data at all; I am not going to show you any mathematical solutions at all; I am just going to talk really in terms of concepts.

In discussing an experimental background for the problem we have two constituent phases at which to look. As regards the fiber phase, in the inorganic fibers such as graphite and boron, these fibers are not known to absorb moisture in any sensible quantities. Organic fibers, on the other hand, such as Kevlar, may be a different matter. Indications are that Kevlar can absorb up to about 7 per cent of its weight in moisture, which is about the same ratio or same amount of moisture absorbancy then as you find in neat epoxy resins.

But if we limit our discussion to high modulus inorganic fibers we can rule out moisture absorption by the fiber. Moisture, however, can be transported through the matrix by capillary action along the fiber matrix interface, by voids, pores, or cracks in the resin system or by diffusion through the resin itself.

Now, under long term exposure to moisture and temperature epoxy resin systems can plasticize, which has been

described earlier today as a reversible process that leads to degradation of mechanical properties. Plasticization does not destroy crosslinking bonds between molecules, as this would create irreversible damage.

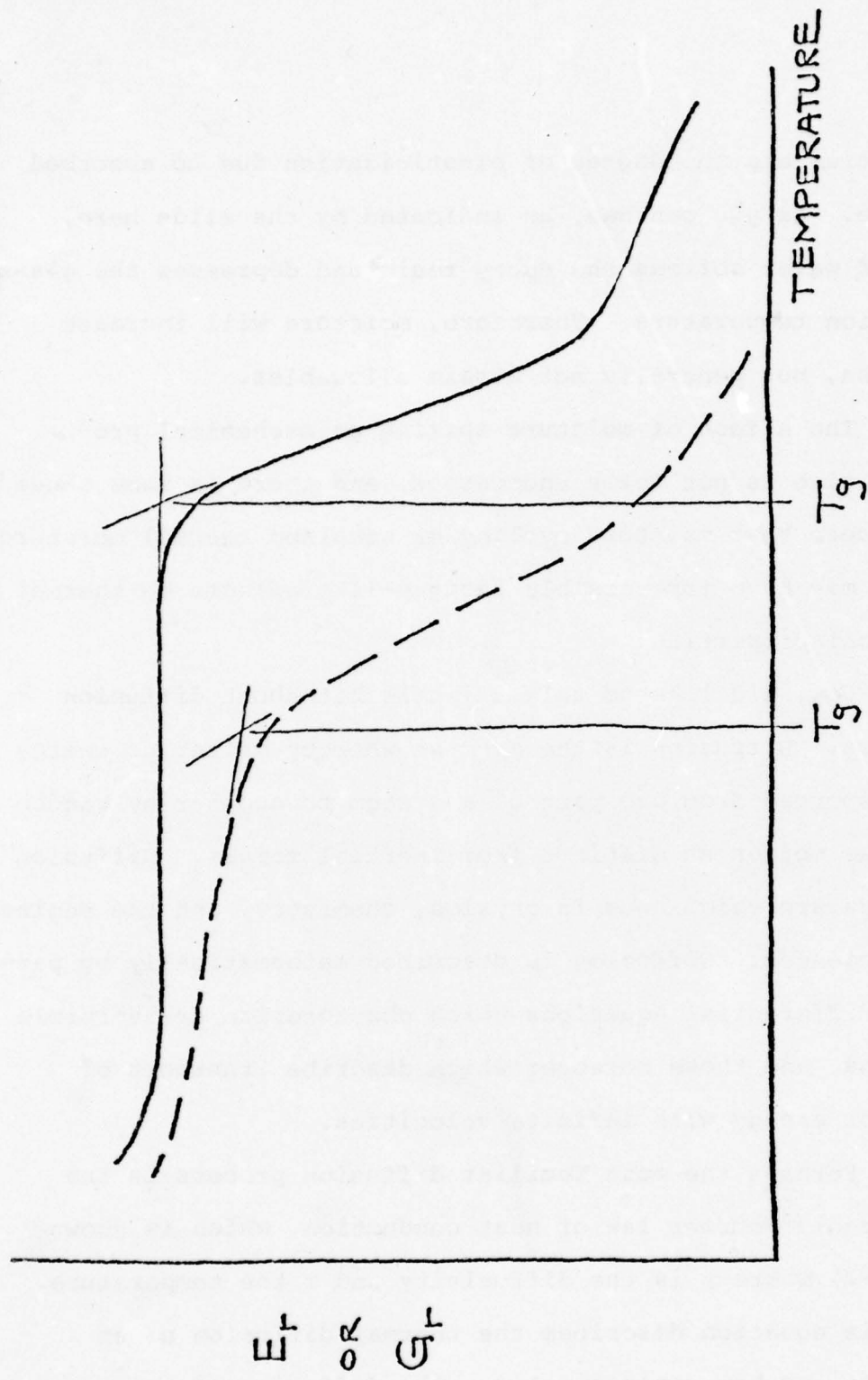
Absorbed moisture has been found to be predominately, if not entirely, water. Lieutenant Charles Sherrell of the Air Force Flight Dynamics Laboratory has some data that show at least 90 per cent of the desorbed products are pure water. The time scale for water absorption by other than artificial environmental conditions is at the order of weeks, and this point has been described in some detail this morning.

Some moisture content is apparently always present. Estimates have been made that between two- and three-tenths of one per cent moisture is present in an epoxy laminate upon immediate removal from the curing oven. Therefore, there is some threshold moisture content that should be presumed always to be present.

The degradation of thermal and mechanical properties as a result of moisturizing the epoxy matrix is really not fully understood. In design practice, property degradation is described in terms of the glass transition temperature T_g of the epoxy.

You might put this slide on, (F-1) although it duplicates something that's been shown earlier, to show how the glass temperature is determined. All polymeric materials have a T_g which is a function of the degree of cross-linking during the curing process, chemical composition, and the length of the

→ INCREASED CURE OR CROSS LINK
 ← INCREASED MOISTURE CONTENT



MOISTURE EFFECTS ON
 GLASS TRANSITION TEMPERATURE T_g

cure cycle, and the degree of plasticization due to absorbed moisture. As you can see, as indicated by the slide here, absorbed water softens the epoxy resin and depresses the glass transition temperature. Therefore, moisture will increase stiffness, but generally not strain allowables.

The effect of moisture spiking on mechanical properties also is not fully understood, and there is some cause for concern that moisture cycling or combined thermal moisture cycling may have irreversible fatigue-like effects on thermal mechanical properties.

Now, I'd like to talk a little bit about diffusion mechanics. Diffusion is the process whereby matter or energy is transported from one part of a system to another by random molecular motion as distinct from inertial forces. Diffusion phenomena are ubiquitous in physics, chemistry, and the engineering sciences. Diffusion is described mathematically by parabolic differential equations which characterize irreversible phenomena, and those moreover which describe transport of matter or energy with infinite velocities.

Perhaps the most familiar diffusion process is the 150-year-old Fourier law of heat conduction, which is shown here (F-2) where χ is the diffusivity and T the temperature. Now, this equation describes the thermal diffusion of an isotropic and homogeneous solid. The diffusion of moisture through a solid is described by equations which are completely analogous to those of heat conduction.

FOURIER LAW

$$\chi \nabla^2 T = \partial T / \partial t$$

MASS CONSERVATION:

$$\nabla F + \partial C / \partial t = 0$$

MOISTURE TRANSFER:

$$F = -D \nabla C$$



$$D \nabla^2 C = \partial C / \partial t$$

FICK'S EQUATION

As a matter of fact, the standard treatise on diffusion, by Crank, is in large part merely a repackaged version of the classic monograph, Conduction of Heat and Solids, by Carslaw and Jaeger, which was written some ten years earlier. Only the notation has been changed to protect the physics. In the language of diffusion we must deal with Fick's equation, which is analogous to the Fourier Law shown above. Fick's equation results from combining the law of mass concentration with the hypothesis that the rate of moisture transfer F is proportional to the gradient of the concentration. Here, F is the transfer of substance per diffusing area, C is the concentration of the diffusing substance, and D is the diffusing coefficient. The negative sign indicates that moisture diffuses from points of higher concentration to points of lower concentration.

When these two basic equations are combined, you come down to the Fick's equation for an isotropic and homogeneous solid. That is, we assume that D is constant. The solution of this equation requires specification of proper and initial boundary conditions in terms of concentration, and several solutions are available for this equation in standard references. I might add that solutions are to be found either in the heat transfer or the diffusion literature, since the equations fundamentally are the same.

However, the physical problem that has brought us here at this Workshop together involves the combined driving forces of temperature and humidity on the diffusion of mois-

ture through solids. We all know what temperature is. Humidity is often described by relative humidity, which is the mass ratio of water vapor content in the air relative to its content at saturation. Relative humidity can be equivalently defined in terms of ratio of vapor pressures and saturation vapor pressure in turn can be related to absolute temperature by some elementary formulas of statistical mechanics.

Now, very little research has been put into developing field equations governing the mutual interaction of moisture and thermal diffusion in solids. I might mention briefly, one elementary model that has been treated by Crank. The physical problem is to calculate the one-dimensional diffusion of heat and moisture in a two-phase medium composed of parallel fibers, separated in this case by air spaces. This problem is similar to that of an epoxy matrix reinforced by continuous unidirectional fibers.

Crank's equations (F-3) take the form as shown on the slide. For diffusion in the X direction, that is in the fiber direction, the four constants here express various combinations of density, fiber volume fraction, specific heat, and heat conductivity. Although this system of equations is perhaps the simplest imaginable for the problem we are addressing, few general solutions are available. Notice the symmetry present in these equations, which emphasizes the similarity between the thermal and the moisture diffusion processes.

Thus far, I have talked about diffusion processes in

CRANK'S EQS. FOR COMBINED
MOISTURE/THERMAL DIFFUSION:

$$D \frac{\partial^2 C}{\partial x^2} - \frac{\partial}{\partial t} (C - \lambda T) = 0$$

$$\rho \frac{\partial^2 T}{\partial x^2} - \frac{\partial}{\partial t} (T - \nu C) = 0$$

isotropic media where Fick's equation governs moisture diffusion independent of temperature. Note that under steady state conditions where the right-hand side vanishes, the concentration gradient must be a harmonic function. This is not the case if we consider anisotropy, which may be due to an oriented constituent phase or to an ordered molecular structure in the solid. In such case, Fick's equation takes the form as shown (F-4) in the second equation here where the D 's now are directionally-dependent constants which are called principal diffusion coefficients.

There has been very little, if anything, done to apply this kind of an analytical approach to filamentary composites. It would seem worthwhile to develop field equations and solutions for layered media, where each ply is referred to a global system of coordinates, much as what has been done in laminated composite theory. Here again, the literature provides little guidance. Crank says nothing about this problem, although Carslaw and Jaeger in their treatise on heat conduction do discuss the mathematically equivalent problem of steady state temperature in anisotropic slabs. The problem is merely discussed, because in the time that problem was treated the computational facilities didn't exist to do very much with it.

Another class of problems that would seem to warrant some attention is that of inhomogeneous media. Consider, for example, moisture diffusion in a medium having a second phase of parallel cylinders where the diffusion takes place in a

$$D \nabla^2 C = \partial C / \partial t$$

$$D_1 \frac{\partial^2 C}{\partial x^2} + D_2 \frac{\partial^2 C}{\partial y^2} + D_3 \frac{\partial^2 C}{\partial z^2} = \partial C / \partial t$$



ANISOTROPIC

$$\frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \partial C / \partial t$$



INHOMOGENEOUS

direction perpendicular to the cylinder axes. This problem is important because it could tell us something about fiber volume and stacking geometry, and provide a realistic micro-mechanical model for diffusion in a composite ply.

Unfortunately, nothing appears to be available either in the diffusion or in the heat conduction literature which addresses this kind of phase geometry and boundary conditions. If this is true of solutions to the Fick's equation for moisture diffusion, imagine how far we are away now from solutions to analogous problems involving interacting diffusion and thermal fields.

The only kind of inhomogeneous media which have been examined (at least to my knowledge) in terms of diffusion mechanics are those for which the inhomogeneity is continuous and monotonically varying. Now if the diffusion coefficient D varies as some nice function like X^n or $(1 + \alpha X)$, or some other relationship of this type, certain solutions are available. But such abstractions don't really appear to me to have very much relevance to the kinds of problems that we are discussing here today.

Throughout our discussion thus far, I have attempted to show the parallel between theories of heat conduction and moisture diffusion. Indeed, even in the pair of equations shown earlier describing interacting thermal and moisture fields in fibrous media, the equations were coupled and symmetric, showing in another way the commonality between these

two phenomena.

At this point, I would like to engage in a little bit of physical speculation. If conduction and diffusion are so closely analogous it seems reasonable to look at the well-developed subject of coupled thermal elasticity for guidance in predicting interaction effects between elastic and moisture fields. After all, the theory of thermal stresses, by that I mean uncoupled thermoelasticity, has recently been successfully applied by Hahn and Pagano to predict residual curing stresses in laminated composite plates due to differential contraction of the matrix and fibers from the cure temperature. Surely, moisture then has some effect on these residual stresses, not to mention its effect on physical and strength properties of the constituent materials, and particularly the neat resin.

Now let us consider for simplicity of illustration the coupled thermoelastic problem in one dimension. If we ignore body and inertial forces, as well as internal heat generation, that is if we confine our attention to quasi-static closed systems, these are equations that govern the problem. (F-5)

Now, if you compare the second of these equations with Fick's equation, you see that they are quite similar. The diffusion coefficient here is analogous to κ , which is a ratio between thermal conductivity and specific heat and the heat conduction problem. The first of these two equations, I might add, is simply the Navier elasticity equation, and the

$$\lambda + 2\mu \frac{\partial e}{\partial x} = \gamma \frac{\partial T}{\partial x}$$

$$\frac{\partial^2 T}{\partial x^2} - \eta \frac{\partial e}{\partial t} = \frac{1}{\kappa} \frac{\partial T}{\partial t}$$

$$\frac{\partial^2 c}{\partial x^2} = \frac{1}{D} \frac{\partial c}{\partial t}$$

THEORETICAL

McKAGUE et al

$$\frac{M_t}{M_\infty} = \frac{4}{L} \sqrt{\frac{Dt}{\pi}}$$

$$\frac{M_t}{M_\infty} = \tanh \left[\frac{4}{L} \sqrt{\frac{Dt}{\pi}} \right]$$

second is basically a statement of the second law of thermodynamics.

Moreover, Fick's equation does not have the term $\eta \dot{e}$, where e is the dilation, which basically couples these two equations.

Now, in the thermoelastic problem the strain and the temperature are coupled and hence the temperature rate affects the mechanical response. In the diffusion problem, since the concentration C is a function of temperature and time, it seems reasonable that C also will affect the mechanical response so that the temperature and concentration, together, affect, and in general will couple with the strain.

The challenge before us, it seems to me, is to derive the fully-coupled equations for strain, temperature and moisture in a thermodynamically open system and examine this system of equations to see when coupling can legitimately be ignored. This challenge is yet to be met. Notice that in the coupled thermoelastic problems the coupling comes about through the term $\eta \dot{e}$ which in fact in almost all cases can quite easily be ignored, because of the time constant η is quite small in those problems. However, this may not be so when introducing moisture diffusion.

I am reminded by some work recently accomplished by Jim Rice and his associates at Brown University concerning deformation of fluid infiltrated media. The field equations they derived are fully analogous to the coupled thermoelastic

equations. But the coupling effect, instead of being generally a second order effect as in most thermoelastic problems, is strongly a first order effect. The message, therefore, is do not be misled by overextended analogies. What may be a second order effect in one problem may be a first order effect in an analogous physical problem.

Now, having touched briefly on the subjects of anisotropy and inhomogeneity and coupled effects in diffusion, I'd like to make just a few closing remarks on non-linear effects.

All natural processes, of course, are nonlinear. The basic question is, how importantly non-linear are they? Everything that we have discussed thus far has concerned linear descriptions of the diffusion problem where causes and effects are proportional and superposition principles apply. Whether or not moisture effects in epoxy resin composites can be adequately described by linear theory is really not presently known, because there is such a scarcity of data to test the limitations of present linear theory.

Some nonlinear descriptions have been proposed, but here again it's not clear how essential the non-linearity was in describing the data or, indeed, even how good the data were to begin with.

I'd like to mention briefly two recent theories which I could call nonlinear. One of these was the one developed by Lee McKague and his colleagues at the Fort Worth Division of General Dynamics. McKague's analysis is based upon an

approximation to the exact solution of Fick's equation for the diffusion of moisture through a thin plate where the two surfaces of the plate are exposed to identical moisture concentrations.

A comparison of the theoretical solution with McKague's empirical approximation is shown in Figure F-5. McKague's solution was constructed so that it would correlate the transient absorption data better, and this has been brought out earlier this afternoon. In particular, the theoretical model did not track their data very well at long times for thin plates when saturation could occur.

I should mention that in their work McKague and his colleagues carried this model much further, primarily by ascribing a temperature dependence to the diffusion coefficient. The important point for us to recognize here, however, is that this particular model is a nonlinear model because it does not satisfy the simple linear Fick's equation. Thus, if one believes the absorption data taken by McKague and his colleagues on T-300 graphite 5208 epoxy resin composites, as I am prepared to do, there is evidence to suggest that a linear model is inadequate for realistic times, temperatures, and humidities. Lee, if you or any of your colleagues are out there, I hope I did you justice by this little commentary.

As a final word on nonlinear effects, I might mention from some recent Soviet work conducted at the Institute of Polymer Mechanics at Latvia, which Jack Weitsman brought to my

attention recently. This work addressed a mutual effect of temperature and humidity on creep, in this case, of polyester. These authors concluded that creep behavior of this polymer exhibited a strong coupling effect between temperature and humidity and that creep could not be expressed by conventional linear creep-type theory.

Since my time is drawing a little bit short, I am going to wind this up. I haven't specifically addressed the problem of strength prediction as a function of absorbed moisture. Indeed, there has been very little done on this problem from a basic mechanics viewpoint. It is clear, however, that strength prediction is intimately associated with absorbency prediction. Without such models, there can be no physically consistent predictive strength model. The strength model involves one further dimension of complication, however, because it is not enough merely to take the constituent strength properties and massage them with the moisture model through some micromechanical manipulation, and churn out time-dependent strength properties. Strength is also closely affected by residual stress fields due to curing stresses and other structural constraints. It seems to me necessary to develop analytical techniques such as the one I mentioned earlier by Hahn and Pagano for calculating internal residual fields, stress and strain fields, for their use in strength prediction models.

In closing, I'd like to summarize briefly the three broad areas (F-6) that I feel from a mechanics vantage are in

GENERAL PROBLEM AREAS

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1. THERMO-MECHANICAL MOISTURE
ABSORPTION THEORY FOR 2-PHASE
LAMINATED COMPOSITES
2. ESTABLISH IMPORTANCE OF
NONLINEAR BEHAVIOR AND
COUPLING (TEMP., STRAIN, MOISTURE)
3. ESTABLISH DESIGN PROPERTIES
MOST SENSITIVE TO MOISTURE

need of some further illumination. The first of these is to develop a physically sound thermo-mechanical theory of moisture absorption in a two-phase composite. This has two immediate uses: first to use as input for a time-dependent theory of strength of epoxy resin composites that can be used in an aircraft fleet maintenance prediction model, and secondly, and perhaps more importantly at this present time, is to enable an accelerated testing schedule to be done in the laboratory and to have some confidence that the accelerated test data are meaningful.

Secondly, from a careful basic level experimental research is needed to determine the importance of nonlinear behavior and coupling effects, if in fact they exist at all, between temperature, strain, and moisture fields.

And, thirdly, additional research should be placed on the design properties that seem to be most closely associated with matrix properties such as compression, shear, fatigue, thermal expansion and dimensional stability problems as a function of temperature and time environments.

Thank you very much for your attention.

DR.MC CULLOUGH: Thank you very much.

We can make allowances for us Texans. We do tend to be a little slower.

The next speaker is Dr. D.H. Kaelble of Rockwell International.

DR. KAELBLE: My talk this afternoon will add, I believe, and illuminate certain aspects of the many of the complications we have heard about both this morning and this afternoon. This study was undertaken with the specific purpose of isolating NDT test methodology and correlating it with strength degradation in a composite system. The study was undertaken as part of the NDT program centered at the Rockwell International and sponsored by the Advanced Projects Research Agency and the Air Force Materials Lab. The study brings to a focus three different parts and three very briefly covered topics in this presentation: the role of the interface, the role of the matrix, and finally the role of a composite system response in terms of the overall moisture effect.

Hygrothermal (separate or combined high moisture and temperature) aging of graphite fiber reinforced epoxy matrix composites produces irreversible deterioration in interlaminar shear strength λ_b over a range of temperatures from $-150^\circ < T < 120^\circ\text{C}$. Fiber surface treatments were employed to produce controlled rates and extents of hydrothermal degradation in the laminated composite. A study was conducted to develop methods of specifically detecting and identifying the extent and mechanism of hydrothermal aging. This study shows that hydrothermal aging concurrently degrades the bonded fiber-matrix interface, produces changes in the chemical network structure of the epoxy matrix, and modifies the differential stress balances imposed by fiber constraints upon the epoxy continuum phase. The degradation state of the fiber-matrix interface is detected

through correlation of surface energetics analysis, ultrasonic characterization, and moisture take up. The state of the bulk epoxy is evaluated by differential scanning calorimetry (DSC) and specific heat measurements, IR and dynamic mechanical spectroscopy, and thermo-mechanical analysis (TMA). The fiber-matrix stress state is delineated by thermal expansivity, dynamic mechanical spectroscopy and ultrasonic response. These nondestructive measurement techniques for hydrothermal aging form the basis for detailed analysis of the relations between materials response and composite performance and reliability.

A number of published reports show that exposure of laminated graphite-epoxy or graphite-polyester composites to water immersion or water vapor at elevated temperatures leads to irreversible degradation of interlaminar shear strength and changes in fracture toughness⁽¹⁻⁶⁾. In this study several recent theories of moisture degradation in composite materials (3-6) were employed in conjunction with a range of nondestructive tests on the composite material to accomplish the following three phases of this program.

1. Prepare and degrade reinforced composite specimens with varied moisture susceptibility.
2. Characterize composites by NDE and correlate with mechanical strength.
3. Develop a mathematical model to relate physical property measurements with molecular mechanisms of moisture degradation.

Experimental

The graphite-epoxy composite materials utilized in this study are described in Table 1. Composite SC-2-2 was designed with a fiber-matrix interface of high moisture sensitivity and composite SC-2-3 was designed to display a moisture resistant interface. The study of the kinetics and mechanisms for hydrothermal aging effects in the interface, bulk matrix, and composite system response are respectively summarized in Table II.

Results

1. Interfacial Aspects

The measurement of interlaminar shear strength (λ_b) and moisture uptake (Wt.%H₂O) served as direct indicators of the rate and extent of moisture degradation. The upper curves of Figure 1 plot the averaged values of λ_b as a function of hydrothermal (100°C in H₂O) aging time while the lower curves display Wt.%H₂O which accompanies strength degradation. The fiber surface treatments described in Table 1 provide widely different kinetics and extent of fractional degradation in interlaminar shear strength in these two composites as shown by upper Figure 1. Analysis of these data is made in terms of the following expression:⁽⁶⁾

$$\lambda_b(t) = \lambda_{b0} [r + (1-r) \exp (-t/\tau)] \quad (1)$$

where $\lambda_b(t)$ and λ_{b0} denote interlaminar shear strength at

TABLE 1

Constituents and Volume Fractions of Components in
Uniaxially Reinforced Graphite-Epoxy Panels

Reinforced Composite Panel	SC-2-2 Moisture Sensitive	SC-2-3 Moisture Resistant
Fiber plys/cm	52	52
Fiber	HTS with Gantrez 169 Size ⁽¹⁾	HTS with Hydrogen Surface Treatment ⁽²⁾
Resin	BP 907	BP 907
<u>Volume Fractions:</u>		
Fiber (%)	59.7	57.0
Resin (%)	38.1	43.0
Voids (%)	2.2	0.1
<u>Densities:</u>		
Fiber P_F (gm/cc)	1.74	1.74
Matrix P_M (gm/cc)	1.21	1.21
Composite P_C (gm/cc)	1.50	1.51

(1) Gantrez 169 is a high molecular weight copolymer of maleic anhydride and methyl vinyl ether applied to the fiber tow from a 1% (by weight) solution in methyl ethyl ketone solvent and dried on the fiber surface.

(2) Graphite HTS fibers heat treated for 120 min at 1038°C in a 90/10:: hydrogen/nitrogen atmosphere.

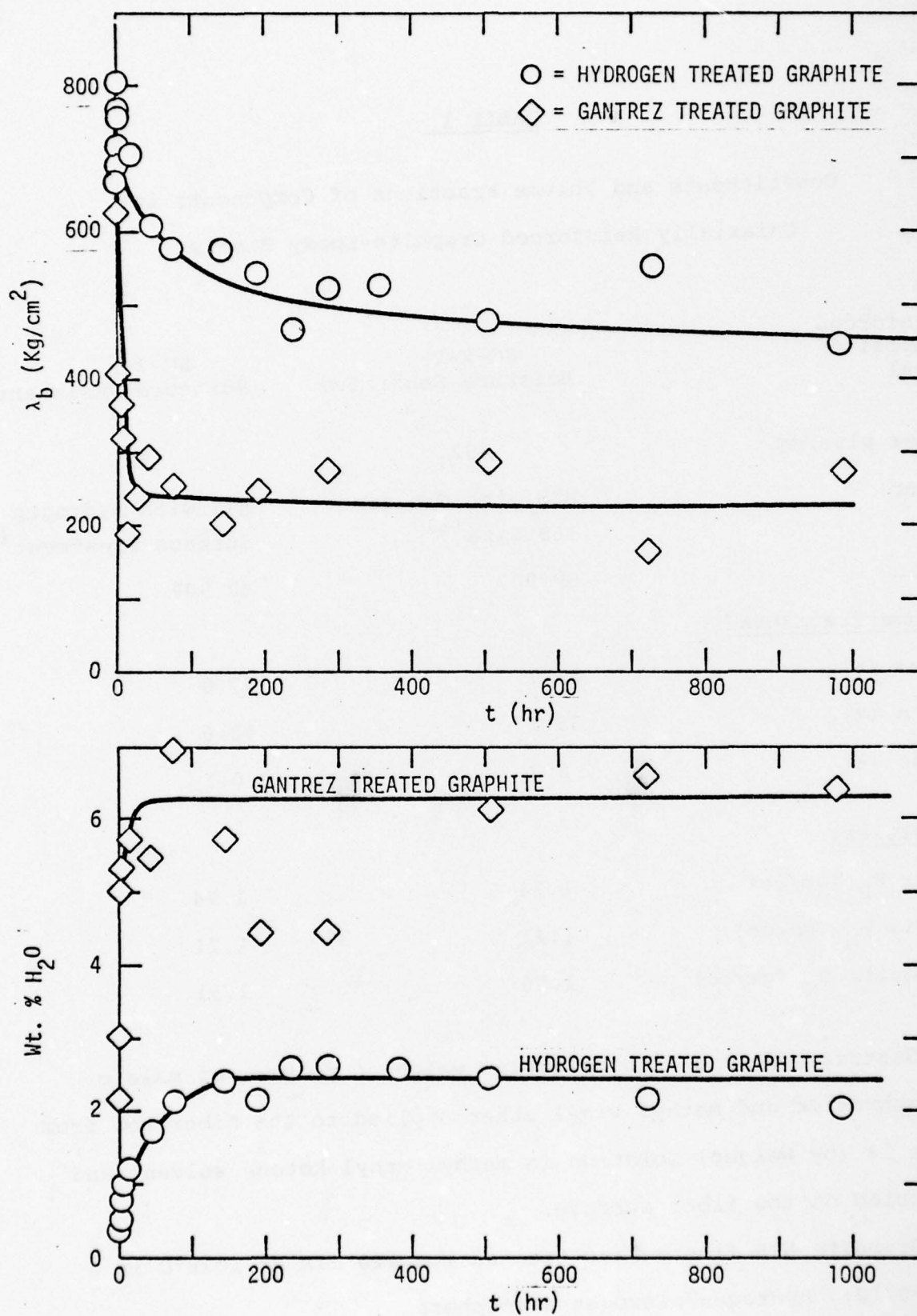


Figure 1

hydrothermal aging time t and $t = 0$ respectively, $r = \lambda_b / \lambda_{b0}$ is a dimensionless degradation ratio and τ the relaxation time for degradation. The moisture sensitivity of composite SC-2-2 is reflected in the low values of $r = 0.37 \pm 0.11$ and $\tau = 3.15 \pm 1.67$ hr as compared to higher values of $r = 0.67 \pm 0.09$ and $\tau = 52.5 \pm 8.9$ hr for moisture resistant composite SC-2-3.

Ultrasonic (2.25 MHz) measurement of longitudinal sound velocity C_L and acoustic absorption α_L at 23°C was conducted on the aged and dried interlaminar shear specimens. The upper curves of Figure 2 show that translaminar sound velocity diminishes in a systematic manner with hydrothermal degradation of shear strength λ_b . The lower curves of Figure 2 show that α_L increases systematically with decreased λ_b . Similar results are obtained for both composite SC-2-2 and SC-2-3 indicating that a single correlation applied for two materials of different interfacial moisture sensitivity.

The data of Figure 1 and Figure 2 represent degradation effects and correlations applicable to ambient test temperature at 23°C. The effect of prior moisture aging and drying of composite SC-2-3 upon λ_b over a range of test temperatures is shown in Figure 3. These data show that the epoxy β relaxation at $T_\beta = -45 \pm 15^\circ\text{C}$ marks the point where λ_b becomes temperature dependent in both aged and unaged composite. The values of λ_b in both unaged and aged composites approach $\lambda_b = 0$ at the matrix glass transition temperature $T_g = 122 \pm 15^\circ\text{C}$. The data of Figure 1 show that λ_b is importantly influenced by matrix structure and that analysis of NDT data on the pure matrix is

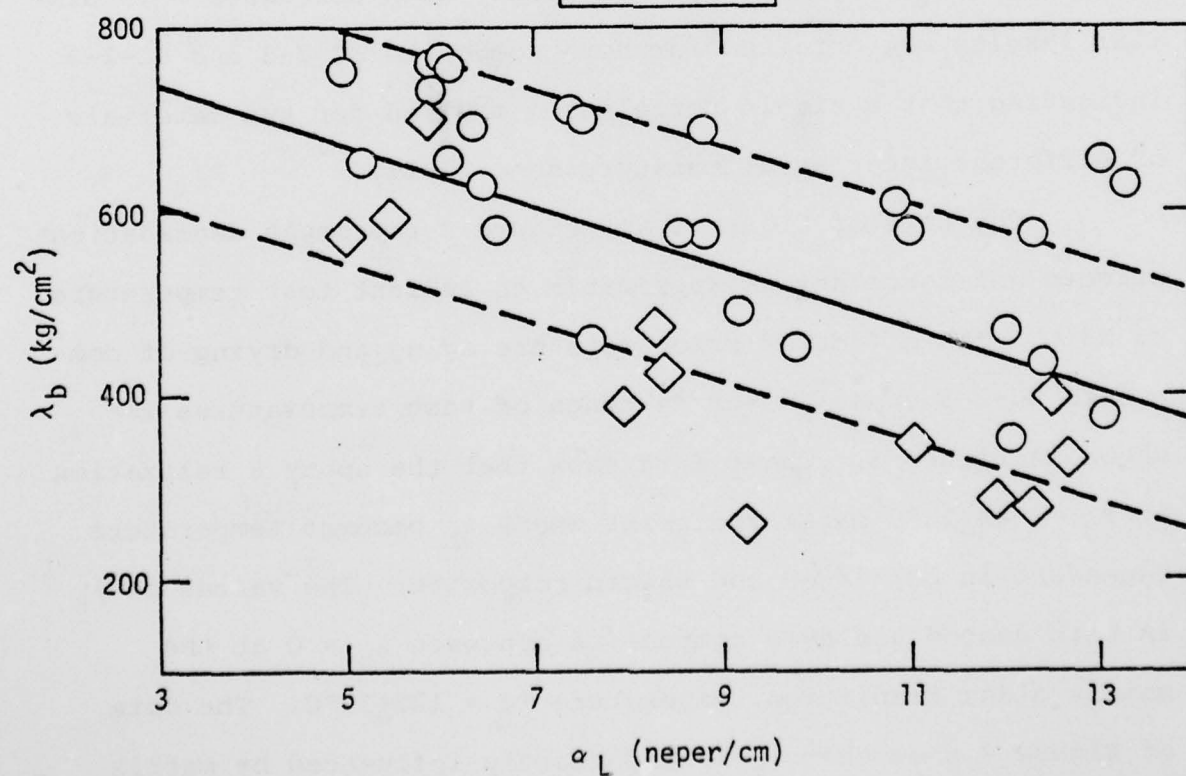
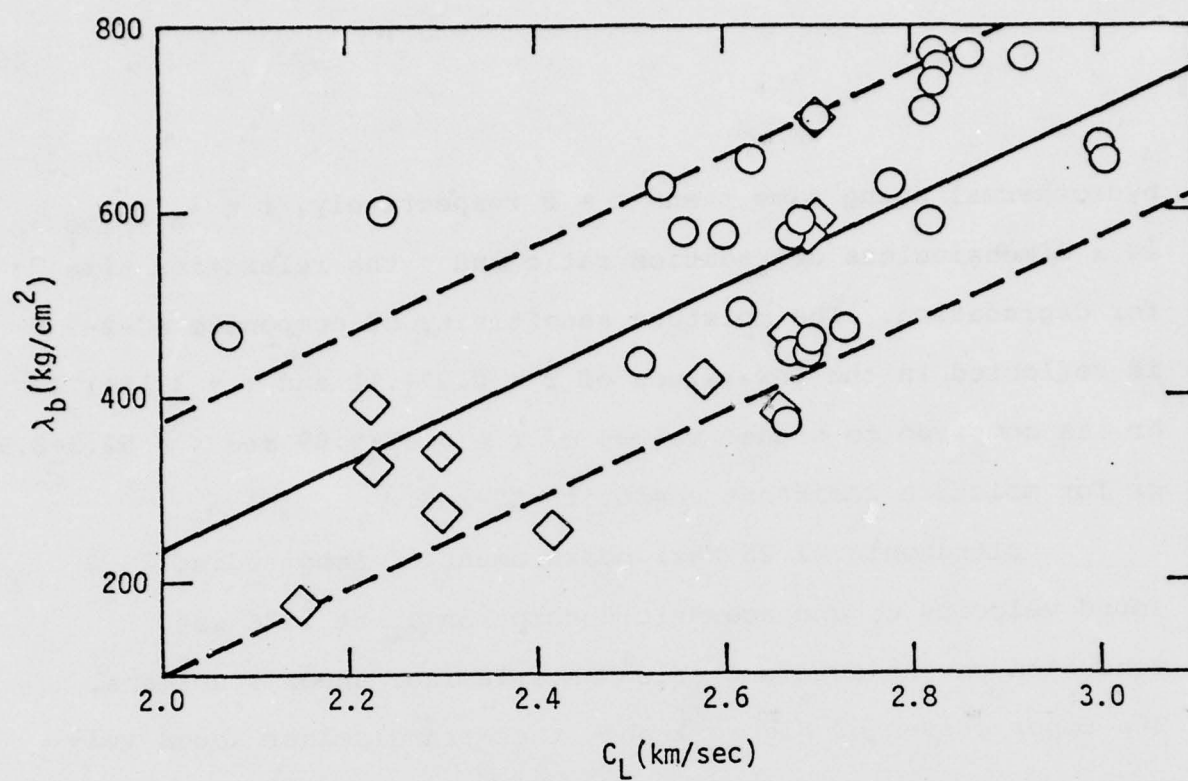


Figure 2

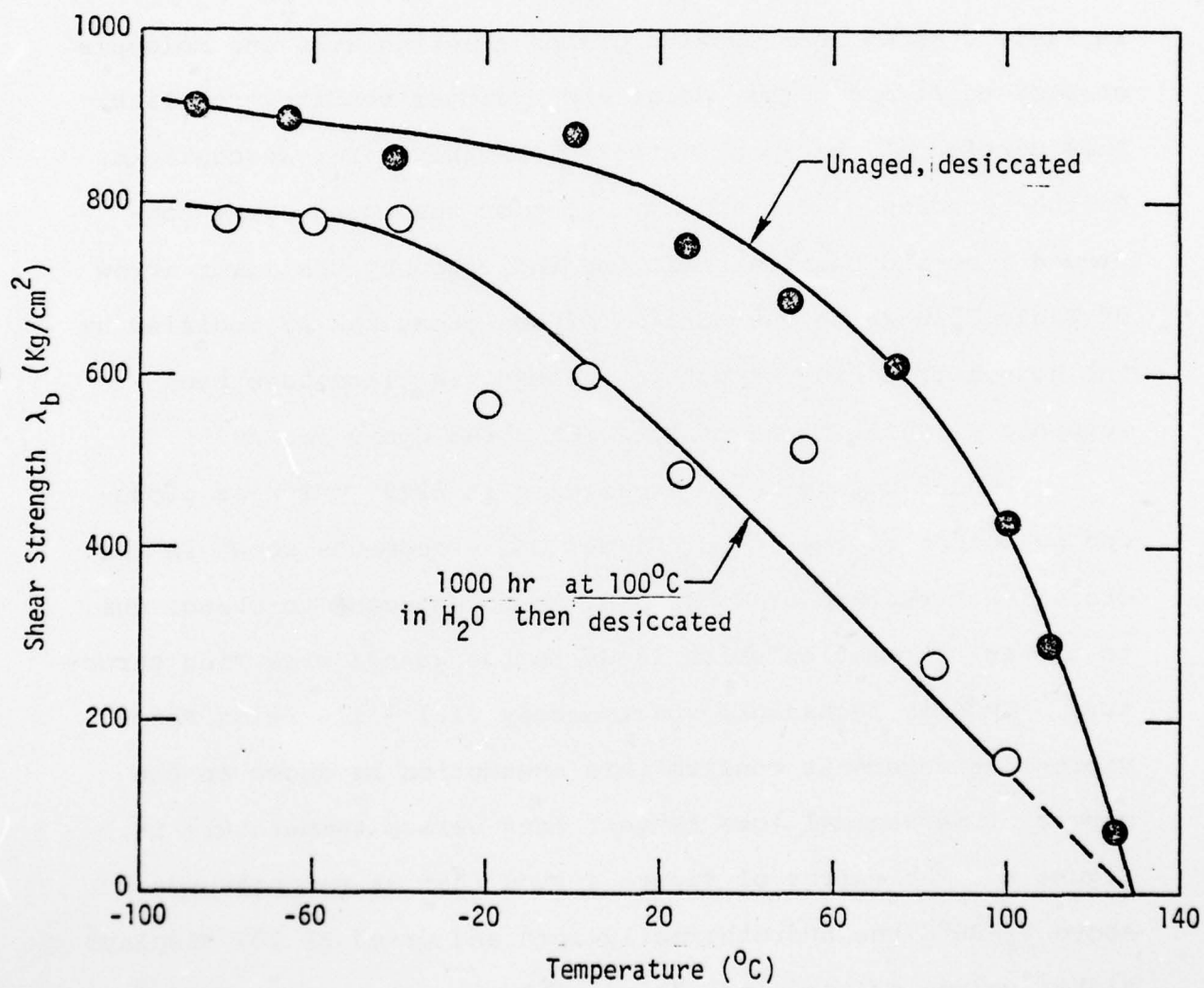


Figure 3

required.

2. Matrix Aspects

A combination of chemical analysis by IR spectroscopy combined with a calorimetry study of curing kinetics indicates that BP 907 epoxy matrix displays the curing mechanisms outlined in Table 3. The first reaction indicated by the upper arrow in Table 3 shows four epoxide groups reacting with one molecule of DICY to form a highly polar and hydrogen bonding crosslink. This portion of the epoxy network is highly water susceptible. Further studies of wet and dry aging of the cured epoxy confirmed a second chemical reaction indicated by the lower arrow of Table 3 in which one portion of the crosslink is modified by the guanyl urea ring structure. These reactions have been reported in the literature for DICY cured epoxy resins^(7,8).

The β viscoelastic transition in BP907 which is produced by motion of the $-O-CH_2-CH(OH)-CH_2-$ segments shown in the crosslink structure of Table 3 might be expected to change due to the aging reaction which leads to the guanyl urea ring structure. Dynamic mechanical spectroscopy (1.1 - 110 Hz on Rheovibron) measurements confirm this assumption as shown in the curves of mechanical loss tangent $\tan\delta$ versus temperature in Figure 4. The curves of Figure 4 show that at temperatures above $T_{\beta}-30^{\circ}\text{C}$ the hydrothermally aged and dried BP 907 displays higher values of $\tan\delta$ indicative of lower values for the modulus of elasticity and sound velocity. These property changes in the pure matrix are consistent with aging effects on

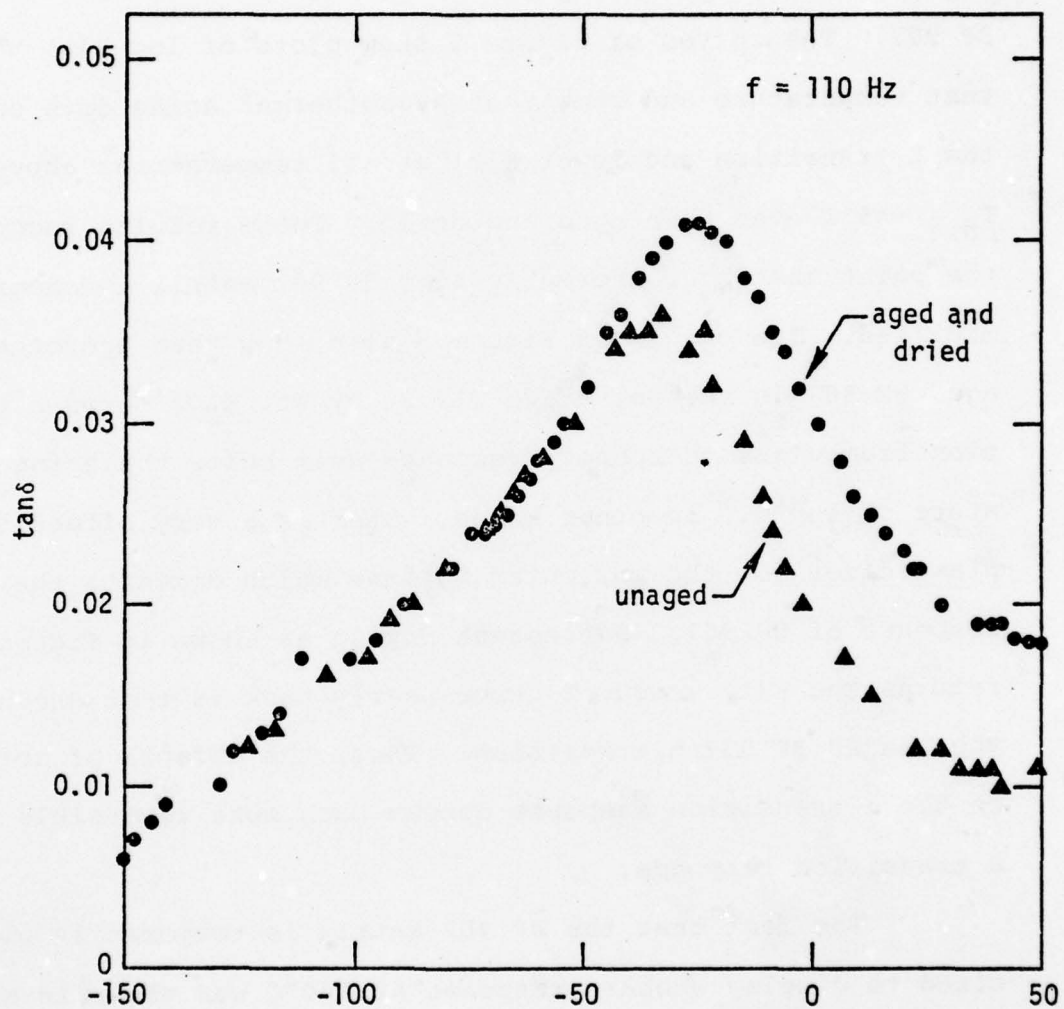


Figure 4

composite ultrasonic response shown in Figure 2.

Measurement of the 15 second tensile relaxation modulus $E(t)$ as a function of test temperature during thermomechanical analysis (TMA)⁽⁹⁾ was undertaken to correlate hydrothermal aging effects on both the β and α (or glass) transitions of BP 907. The curves of Figure 5 show plots of $\log E(t)$ versus test temperature and show that hydrothermal aging does enhance the β transition and lower $E(t)$ at all temperatures above $T_{\beta} \approx -45^{\circ}\text{C}$ even when aged and dried. These results reconfirm the point that hydrothermally aged BP 907 matrix is chemically modified. The curves of Figure 5 also show that hydrothermally aged BP 907 in the wet state (12.2% by Wt. H_2O) shows a transition from glass to rubbery response well below the aging temperature of 100°C . In other words, water is a very effective plasticizer for the molecular motions which dominate the T_g response of BP 907. Subsequent drying as shown in Figure 5 returns the $E(t)$ versus T curve nearly back to that shown for the unaged BP 907 α transition. Thus, the effects of moisture on the α transition response appear much more reversible than for β transition response.

The fact that the BP 907 matrix is temporarily plasticized to display rubbery response at 100°C was shown in subsequent studies to stimulate the growth of defects in the bulk resin which substantially lower the cohesive fracture toughness. All of the aging effects discussed above for the pure matrix phase contribute to the overall changes in composite

interlaminar shear strength as reported in Figure 1 and Figure 3. The temperature dependence of λ_b in Figure 3 is clearly correlated with the $E(t)$ versus T functions of the pure BP907 shown in Figure 5.

3. Composite System Response

Fabrication of polymer composite laminates invariably involves temperature differentials of over 100°C wherein significant internal (curing) stresses are developed within the composite. In some cases, these stresses are reported to cause interlaminar failure or modified thermal expansivity. (10-14) In this study, we observe what appears to be a new and important internal stress effect evidently produced by the specific history of hydrothermal aging. When composite SC-2-2 and SC-2-3 are hydrothermally aged at 100°C in H_2O the curves of Figure 5 show that the matrix achieves a rubbery state where $T_g < 100^\circ C$. These swollen samples are removed to 23°C in the swollen state and thus the swollen matrix is returned to a glass state where $T_g > 23^\circ C$. Subsequent desiccation removes the water from the glassy matrix and evidently this drying process leaves a state of excess free volume in the matrix phase. The internal stresses produced by this moisture uptake and drying cycle are sufficient to produce interlaminar failure in moisture sensitive composite SC-2-2. In moisture resistant composite SC-2-3 failure was not observed but large hysteresis in thermal strain versus temperature functions and suppression of the α transition temperature are clear evidence of the excess free volume state

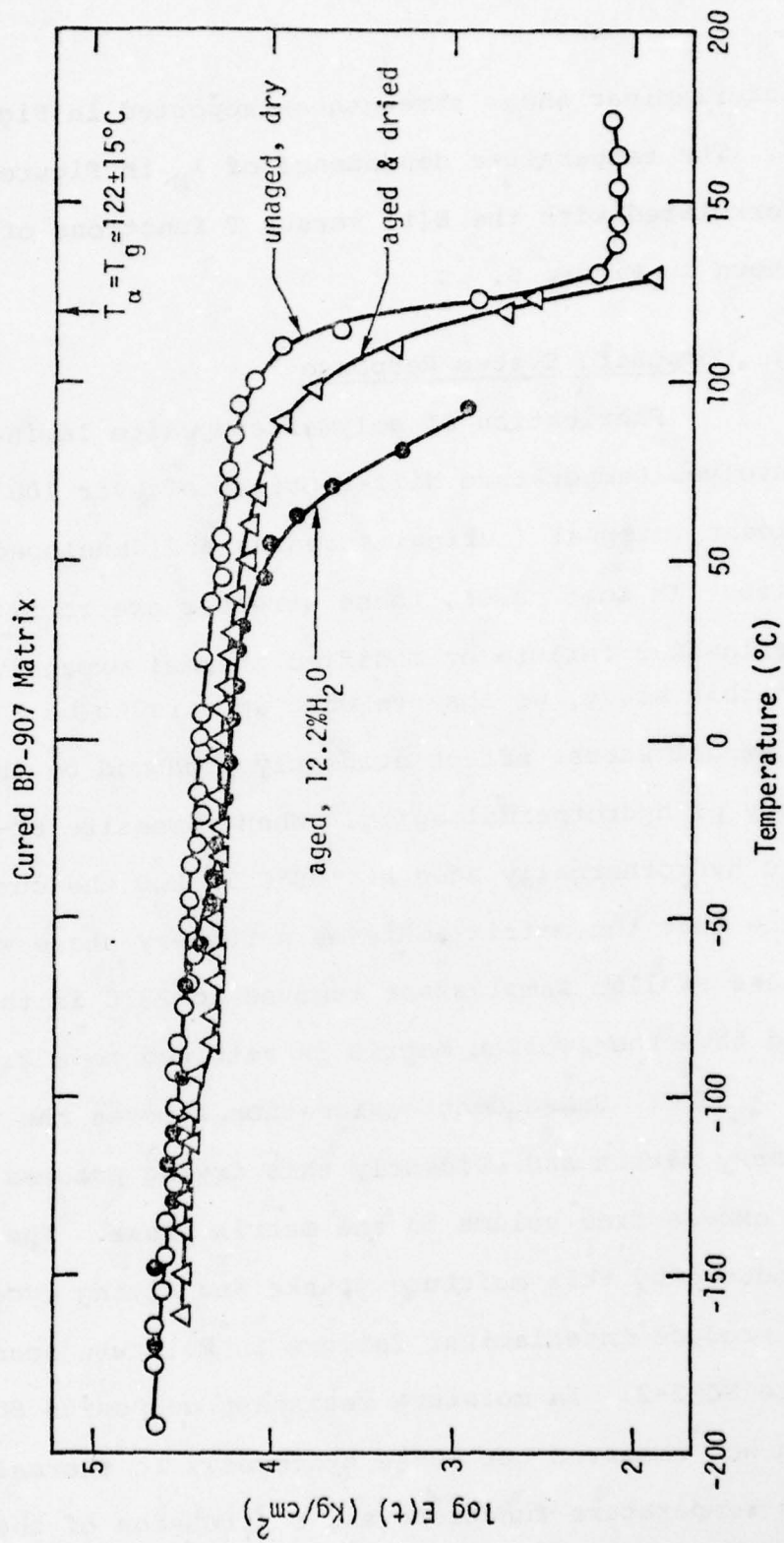


Figure 5

which correlates with a high triaxial tensile stress in the matrix phase.

Measurement of linear thermal strain response curves are illustrated in Figure 6 for composite SC-2-3 which is hydrothermally aged and dried at 23°C. The upper left curve shows the change in length, where initial length $L_0 = 1.000$ in, by first cooling to -95°C then heating to 170°C at constant thermal scan rate $\pm 1^\circ$ c/min and transverse to the fibers. At about +80°C on the first thermal cycle the curve bends downward and on cooling to 23°C a 0.6% loss in sample length is evident due to free volume collapse in the matrix phase.

The second thermal cycle shown in the upper right portion of Figure 6 still shows evidence of volume collapse accompanied by the expected change in slope at about 100°C characteristics of normal glass transition response for the BP 907 matrix. The third thermal cycle shown in the lower portion of Figure 6 shows that the hysteresis behavior has been essentially removed by the thermal annealing above T_g and the BP 907 displays a normal change in thermal expansivity at $T_g > 100^\circ\text{C}$.

The multiple curves of Figure 7 display the results of dynamic mechanical (Rheovibron) measurement of $\tan\delta$ at 110 Hz in the fiber axis of the composite. The first, second and third thermal scans (respective data symbols - closed square, closed circle, closed triangle) show successive shifts of the α transition curves of \tan versus T to higher temperature. The first thermal scan of the hydrothermally aged and dried specimen

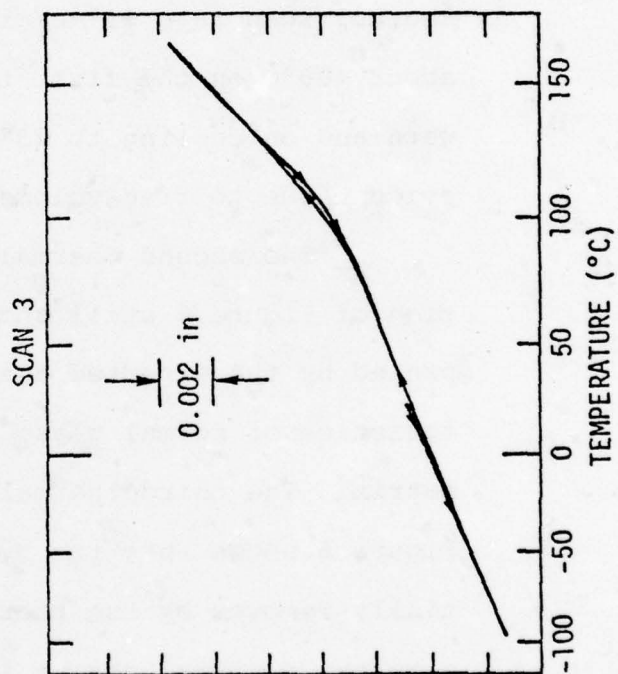
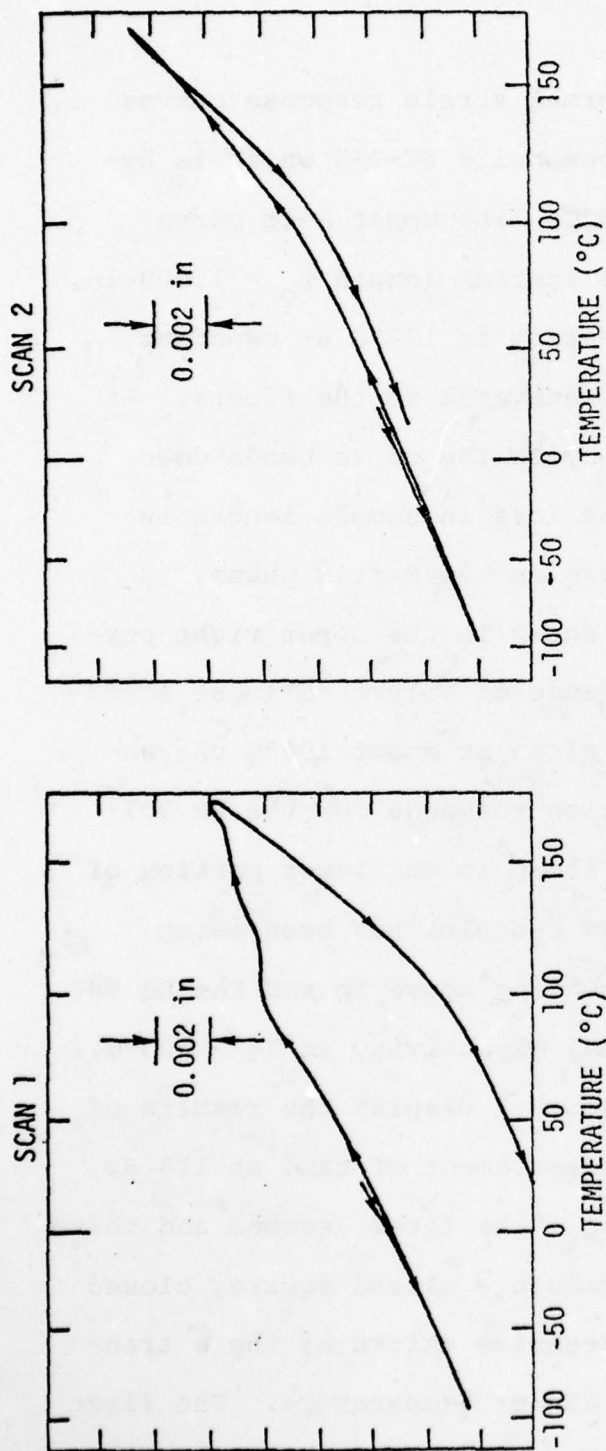


Figure 6

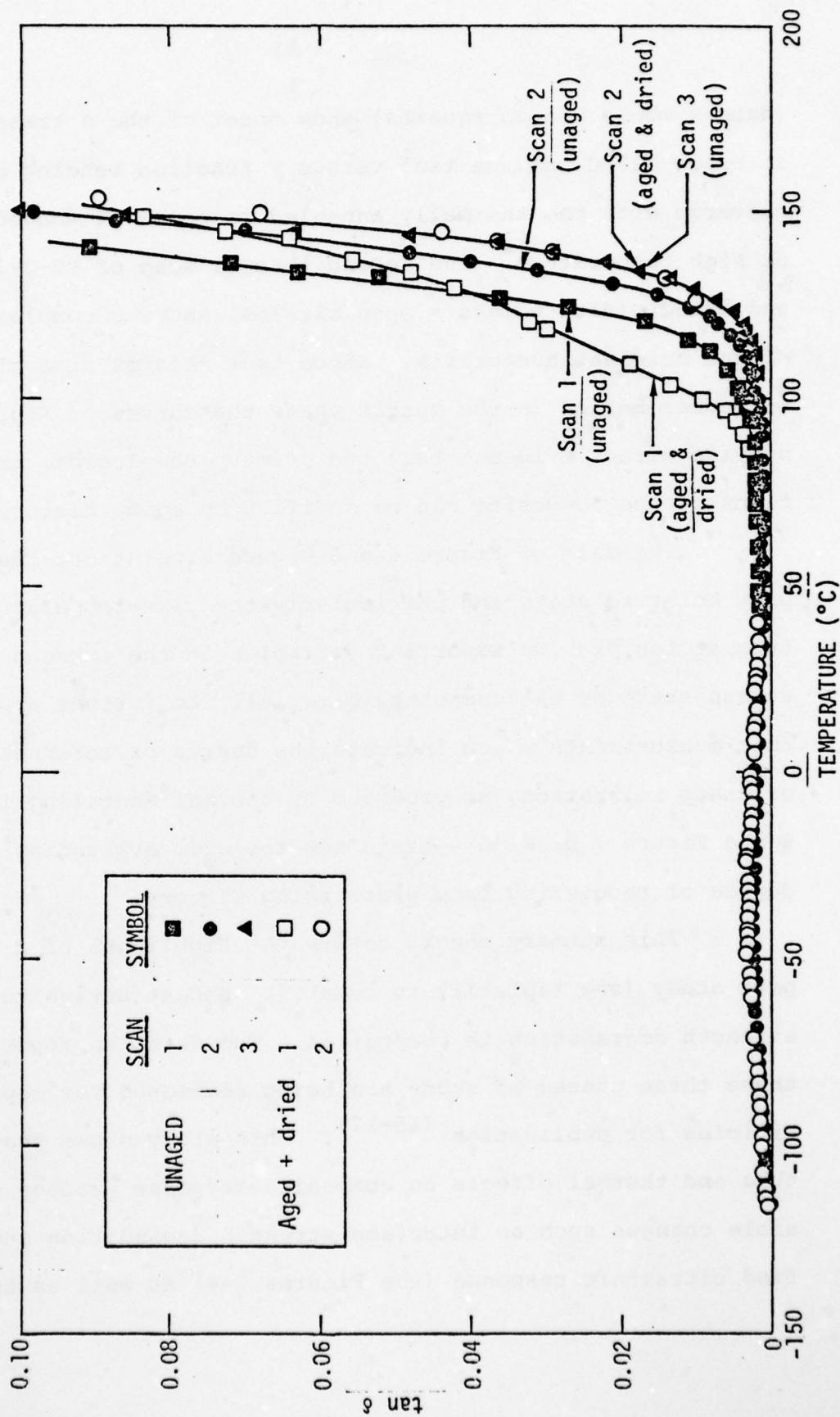


Figure 7

(data symbols = open squares) show onset of the α transition at below 100°C and the $\tan\delta$ versus T function bending over to converge with the thermally annealed response of unaged SC-2-3 at high temperature. The second thermal scan of SC-2-3, aged and dried, (data points = open circles) shows a complete loss of the original hysteresis. Since $\tan\delta$ relates directly with molecular motion in the matrix phase the curves of Figure 7 provide direct evidence that the primary rheological transitions of the composite can be modified by aging history.

The data of Figure 6 and Figure 7 point out that the past moisture state and particularly the time-temperature-moisture states provide important variables in the current internal stress state of the composite material. It further appears that measurements which indicate the degree of internal stress or creep relaxation, as produced by thermal annealing in Figure 6 and Figure 7 provide a basic new tool for evaluating the degree of recovering from prior aging history.

This summary report covers the highlights of a three-part study (see Table II) to identify nondestructive tests for strength degradation in composites. The detailed reports of these three phases of study are being developed for separate articles for publication (15-17). This study shows that moisture and thermal effects on composite response produce irreversible changes such as interface strength degradation and modified ultrasonic response (see Figures 2-4) as well as temporary

TABLE 2

Experimental Methods for Study of Moisture
Degradation

Part 1: Interface

Surface energy analysis
Interlaminar shear strength
Moisture take up
Ultrasonics-transverse (2.25 MHz)
SEM failure surface

Part 2: Bulk Matrix

Differential scanning calorimetry
Specific heat
Infrared spectroscopy
Dynamic mechanical spectroscopy (1.1-110 Hz)
Thermomechanical analysis
SEM failure surface

Part 3: Composite System Response

Thermal expansivity
Dynamic mechanical spectroscopy (1.1-110 Hz)
Ultrasonics - longitudinal (30 KHz)
Ultrasonics - transverse (1-10 MHz)
SEM failure surface

frozen in stress states (see Figures 6-7) which can be removed by thermal annealing above T_g . It would appear that separation of irreversible and reversible aging effects in one important aspect of nondestructive evaluation (NDE). It further appears that in composites a thorough knowledge of the physiochemical processes as obtained by interface and bulk matrix studies which form Part 1 and Part 2 of this program will always be a prerequisite to diagnostic NDE of aging and strength degradation in the composite part.

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DELAWARE UNIV NEWARK CENTER FOR COMPOSITE MATERIALS

F/G 11/4

THE EFFECTS OF RELATIVE HUMIDITY AND ELEVATED TEMPERATURE ON CO--ETC(U)

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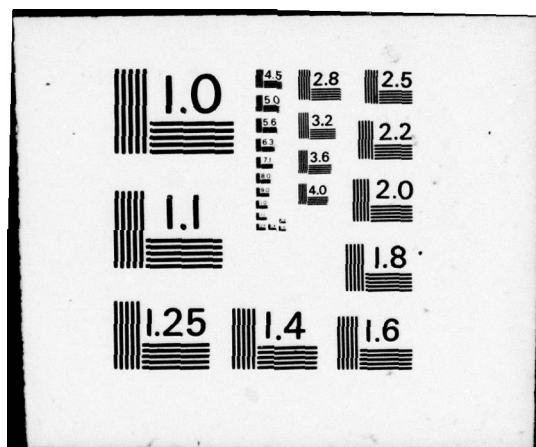
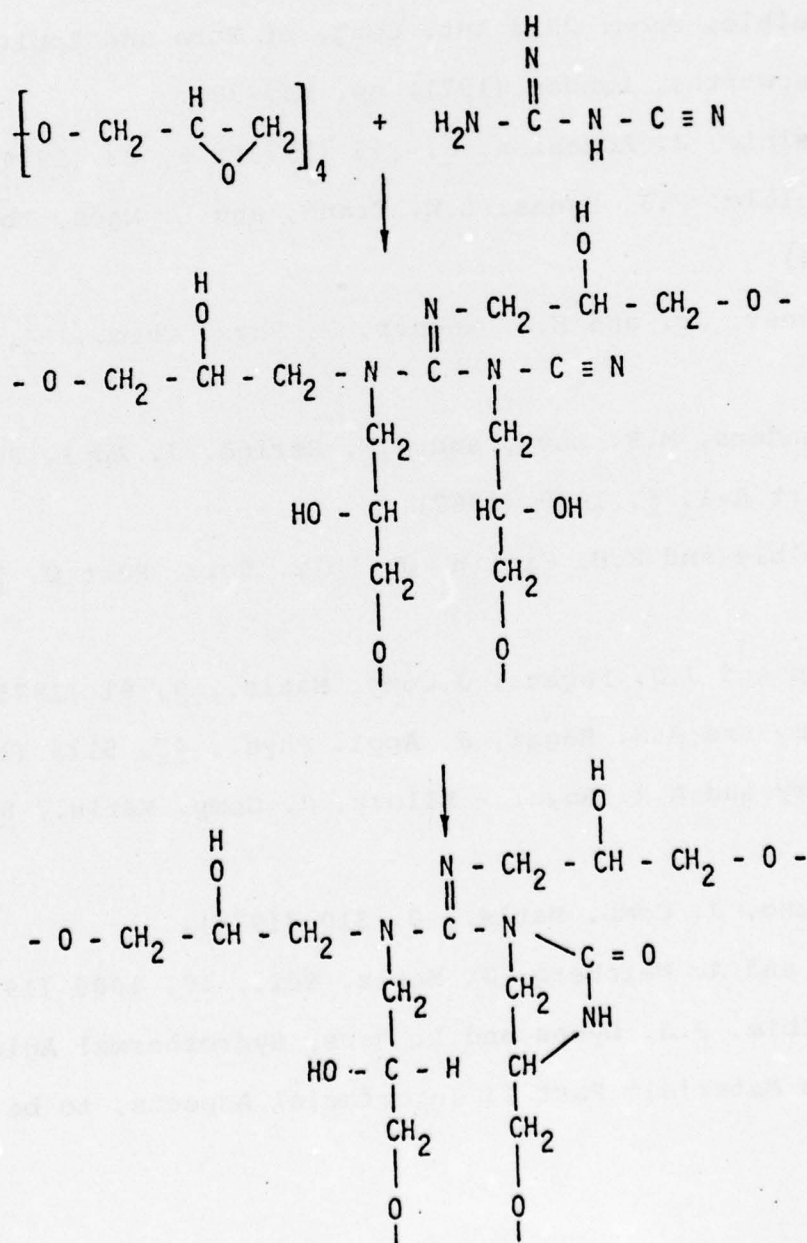


TABLE 3

Suggested Curing Mechanism for Epoxy BP907 Resin

Epoxy + Dicyanodiamide (DICY)



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DR. MCCULLOUGH: Thank you very much. Our next speaker in the session on failure processes is R.H. Patrick, University of Pittsburgh.

3. Failure Processes

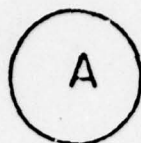
DR. PATRICK: I have been intrigued by the discussion today inasmuch as I'm primarily interested in adhesion, and I look upon a composite as one horrendous mess of adhesive bonds. It's terribly complex, and I think one of the major approaches -- as a matter of fact it's interesting, I have been debating on what approach to take in this discussion, since Bill Walker first called me, and I am going to perhaps do a little bit of preaching, because it seems to me that one of the major problems that we have in something as complex as a composite is the fact that how in the world does one really know where one is? I think Dave Kaelble does some of the neatest work that is done in this area. Normally, I wouldn't give Dave a pat, but he deserves it, poor fellow, and I think that it's clearly evident that so much of the work that's done -- George Thomas this morning pointed out the contradictions that one can get evaluating and analyzing composite systems.

Very frequently they are totally out of control. I, myself, prefer to as much as possible work with a model system until one can determine where you are and then build on that.

In that regard, I would like to very briefly run through some work that has been done by ourselves and by some others that has to do with model systems.

Now, the first one (Figure 1). This picture you have seen a thousand times, but anybody who has a scanning microscope available to him and who would fracture a composite, but I throw it up there to show we don't ever do things crudely but occasionally classically simply. So this is a classically simple description of a liquid phase reacting with a fiber cross-section which can either be a rough surface or a smooth surface. Normally, one would anticipate that the surface would be in some fashion surrounded by the liquid, and then we develop an interface or as Bickerman would say, interphase, and this would represent either orientation, morphological and chemical reactions and a number of other things occurring in the interface.

Now, in a composite of a liquid phase plus the fibrous phase, this is deathless art, I would point out, don't look at the term metal, that's out of there -- we are poverty-stricken in Pittsburgh so we have to use this for many things -- the liquid can surround -- the simplest case would simply be the liquid surrounding the fiber. Normally, this will dilute the system and cause problems as far as the overall strength of the system is concerned, even as though if you could pull each one of the fibers out individually you would have a system with just some vertical holes or relatively vertical holes.



LIQUID PHASE

282

SOLID
PHASE



INTERFACIAL INTERACTION
OF A LIQUID AND A FIBER

INTERPHASE MATERIAL
(MORPHOLOGICAL,
CHEMICAL,
PHYSICAL, ETC)

FIGURE 1.

Secondly, there can be a physical inclusion, this, incidentally, the area out here represents the matrix itself where we have a physical inclusion, some sort of interaction, probably due to wetting of the filter, in this case the fiber by the matrix, this generally stiffens the system. There may be a tensile increase but there may not. Better the system where we have physisorption of the material, the material has now come within molecular atomic differences and we physisorb the material and get a marked overall improvement in the strength. However, these sorts of interactions are very often susceptible to, as we well know, moisture, and environmental, things of that nature, thermal excursions and the like. People say, and it's a quote, "they say,"because, in my mind, seldom has this been proven, that there is sometimes chemical interaction as an interface in which there is chemical absorption of a material in which covalent, surface covalent, or ionic bonds, are formed at the interface. I am not sure. Walter Winchell isn't sure that this is the ideal situation because we haven't it proven, at least to my mind we haven't.

There are those, too, who would argue this point.

The next, (Figure 2) some very specific points here for a second, we will skip over it very fast, this would represent a shrink fit. These would represent primary, the fourth stage of the view graph before, in which you actually form this sort of an atomic structure, then we have the

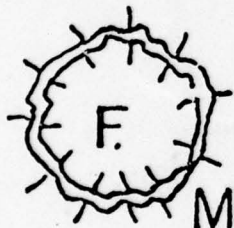
SCHEMATIC OF MATRIX FILLER INTERACTIONS



1. PHYSICAL INCLUSION IN A METAL MATRIX,
M. WEAKENS SYSTEM, ACTS AS A DILUENT.



2. PHYSICAL INCLUSION AND WETTING OF
FILLER BY MATRIX, SOME STIFFENING WITH
INCREASE IN TENSILE AND DECREASE IN
ELONGATION.



3. PHYSORPTION OF MATRIX ONTO FILLER
SURFACE, MARKED OVERALL STRENGTHENING.



4. CHEMISORPTION OF MATRIX ONTO FILLER
SURFACE, COVALENT OR IONIC BONDS.

F=FILLER M=MATRIX

FIGURE 2.

secondary types, disproportion, primary bonding, the dipole, dipoles. This is relatively easy to obtain. This is difficult to obtain.

In regard to the primary bonding and the secondary bonding, this would represent 6.6 electron volts and this is about 1.6. This would be the secondary bonding, which would give theoretically 94,000 p.s.i. if one converts that to a force, and 9.4 million in the case of primary bonding. I have seldom seen -- even David has not seen 9.4 million tensile, right? But this is theoretically what one could obtain. Obviously, there are so many things that prevent this that we won't even discuss that.

Now, have we got that thing fired up? Okay.

Can you see that? This is a classic slide that everybody shows in which we have the fracture of a typical composite. I think the thing that we should think about here is we have situations -- this, incidentally, was a finished -- it had a xylene finish on the glass and we see areas where there is virtually no resin around the glass at all and it has been pulled out of the holes just as neat as can be.

The next slide, I think, is a little higher magnification and you can see that this is really -- can you see that back there? How does one analyze a thing like this if you break this and start breaking it down into units of failure? It's extremely difficult. Please note that this fiber which comes up in this direction seems to be very well coated with the resin in the failure system. How come you

have got one end which is literally slipping out like a greased pig and another one in which you have obviously taken a great deal of energy to cause that failure to occur?

Next slide. This is deathless art and I wouldn't want you to miss it. We wanted to examine the effect of a xylene finish as it functioned in a laminate in proving its resistance to an aqueous environment, either water vapor or liquid water, and in order to do this we tried to do it with a composite and got totally lost, as you can easily imagine. So we decided the best approach would be to make a little button, through the button to place a glass fiber, in this case we actually used a 0.04 rod which was freshly drawn in a zero or less than one part per million water vapor atmosphere. The little button with the rod poking through it was made in the dry box under those conditions in dry nitrogen, and then we sealed it to a glass envelope in which we had placed tritiated water. The concept was that if we indeed had -- oh, we compared this with this one in which there was no glass rod, to make sure that we were not going to get transport of the water -- I don't use the word, diffusion, because I don't know what the mechanism is -- the water through the button itself, because on the top of the button we placed a photographic emulsion, a floated emulsion, and this worked quite nice.

The next slide. Don't pay attention to this one. This represents an actual specimen. We let the rod go

through farther than normal just so that you could see where it was. Here it represents the button which is about 0.030 in. thick. This is looking down through the top. Those are simply positioning lugs inside. And then, of course, we had put the tritiated water and floated the emulsion on top, and as a function of time we observed the interaction of the tritiated water, the radioactive material and the photographic emulsion.

Now, the next slide, this is sort of faked a little bit, in which we ground off the top of the rod so that you could see it better. It's hard to see otherwise. And this is just the shadow within the button itself. These are the mounting lugs and the tubes on the outside.

Next slide is a typical specimen in which we developed the photographic film, and here you will notice is the shadow that is caused by the interaction of the tritiated water with the emulsion, the precipitate silver. I had the bright concept that I was going to hire a high school kid and he was going to look through the microscope and count all the little particles of silver, which you can do if you had -- you would have to have infinite patience. The kid gave up after about an hour and a half, because it takes about a hundred events, radioactive events, to cause precipitation of one grain of silver. It's simple arithmetic. Even I could do that. I could figure out how many particles, how much water was diffusing through. We gave

that up as a very bad job and the Navy simply wouldn't pay us for the time. We simply did this on the basis of did we or did we not get transport through the interface.

Next slide.

At any rate, we got the situation where it was clear that whenever we had xylene on the glass rod -- I will tell you how we did it. I wish I had the slide. I don't know how I missed it. We use an anhydrous glass rod, which was a rod which never saw any water vapor at all, made into the button, and found that it would not transport water in six months through the interface. Now, mind you, this was either water vapor, which was simply by having the button on the top, or liquid water, by inverting it. We didn't transport any water through the interface when we had no xylene present.

Finally, if we finished the glass with A-1100, and this was specially prepared A-1100 that Union Carbide made for us so the purity was very high, we had very small vials, only used it once, we went all through that rubbish that you would anticipate that a moderately careful investigator would do, and found that if we saturated the rod prior to putting the finish on, after putting the finish on, let the rod stay out in the laboratory air, did all sorts of nasty things to it, only when we had xylene finisher on the glass rod could we get transport of water through the interface.

Now, this doesn't seem to make a lot of sense, because people do that dreadful test which I abhor and they call it the water boil test and they find that the flex strength of the composites is markedly improved by the addition of xylene finish, to which I say, okay, what the xylene finish must be doing is functioning in a mechanical way and preventing, in taking up the stresses within this spongy, cheesy, material, small as it is, and that we find that this seems to do the job quite well.

Okay. When one adds the xylene to epoxy resin, incidentally, in spite of what the people at Union Carbide say, this does not function the same way.

Okay. Now, how do failures occur in the composite?

We will give this a very fast shot. This is some work which was done by our own company, Alpha, and Mostavoy and Ripley at the research laboratory, and this concerns the failure, interfacial failure under what I prefer to call stress solvolytic conditions, and they just refer to it as stress corrosion, but I would prefer the fact that the bond is solvolyzed due to the presence of the water vapor.

The next slide.

This is the specimen that was used, however, it was surrounded by glass -- it was glass beam surrounded by a well in which water was placed, and then a static load was hung on the beam and the next slide, this is a schematic, this is Mostavoy and Ripley, I should point out, in which

the precrack that represents the ends of the beam, there was a precrack in the bond, you say this doesn't look like a composite, but it really is a composite except it happened to be a gross one, we removed the adherend for the sake of seeing what was going on, and you can see schematically this represents only the bond itself in that the precrack is in the center of the bond, and that either side somewhere in the vicinity of -- if one imagined a stress field around the cracked tip on either side, at the interface of the glass and the resin, a failure starts to occur. This is interfacial, now, and there is no joining of this cracked tip, which is the big flaw in the system, that is put there by the workers, these are not involved in it, and this continues to grow as long as a stress is applied to this system until such time as it joins up, and then it will transfer along the interface, and the failure, of course, then gets very gross.

Simultaneously, a failure can start above, which is independent, this is on the top -- this would be substrate up above, substrate underneath, so that you can have two cracks proceeding independent of one another as the stresses continue to be applied to this system.

Now the same thing can occur in a composite system. If we have a system that is under stress, water is allowed to ingress into the system in some fashion, and I'm not going to argue as to how this will occur. We know that it

proceeds rather slowly through the bulk of the material. I think that is self-evident from the comments that we heard earlier this morning, from ships. These things are stuck in the water and left there and they seem to work really quite well and one would think that they should fail, because there is enough water in the ocean to cause all sorts of problems. But they don't seem to. So apparently there has to be some way that the water gets into the interface. We have a singularity, of course, here at the corner of the substrate and the resin itself.

Okay. Now, what else did I want to cover?

What is the next slide that we have there?

Oh, this is -- this happens to be a schematic of a system in which they happened to be aluminum beams with an epoxy resin, the same failure occurs. As a matter of fact that occurs somewhat more rapidly with glass substrates, and this is just an indication that we literally had a tongue of adhesive which we broke off and looked at. But that we had superstrate and substrate failure at the interface in this particular case.

Okay. Now the next slide.

I think another point that can be made concerning composites is some interesting work that Kenyon and I don't know whether DeBenedetto was involved in there or not, but Kenyon in St. Louis found that if he had -- he was working with glass beads -- if he coated the glass beads -- if we had a little better focus on the bottom of that it would be

helpful -- this is just a xylene without a functional group, and we find that as the volume percent of the beads goes up that the strength goes down rather dramatically. As a matter of fact at 20 volume percent and down at a factor of 2 from 11 down about 5.

However, this is the material by itself that just fails, degenerates in value as the volume percent of the glass spheres increases.

Now, unfortunately, there is not a whole curve for this, but there were three or four specimens in which he coated the glass beads with a rubber layer and, lo and behold, that their volume percent considerably better than the beads which were untreated, and then with a xylene treatment he found that this happens to be A-187, which I can't remember -- is that the acryloxy, or is that oxy ring -- regardless it was the xylene, that it improved rather markedly as the up to 50 volume percent.

Lo and behold, when he first treated with a rubber layer plus and then added the A-1100, and, unfortunately, these are the things that happen experimentally, these are not the same xylenes, which is really a shame, he found that there was an improvement in the strength of the material. One hardly thinks of glass beads as being reinforcing, glass spheres, but he managed to, by adding a controlled stress absorbing layer in the interface, he managed to improve the situation.

Now, we talk about advanced composites and what the advanced composites can do for us. Unfortunately, the technology having to do with the glass resin composites ran far ahead of where we really knew what was going on. As a matter of fact, I don't think we really caught up until this point, and it would be shameful if the same thing should happen with graphite reinforced systems. I think we have to find out what is going on.

Now, there has been a modicum of work going on in the country concerning graphite, graphite interfaces, the surfaces of graphite, and this sort of thing, but I feel there has to be more and there has to be some genuine understanding of where we are, because it turns out amazingly enough that even if you use graphite in aluminum matrices that environment, namely, God's cruelest liquid, water, raises hell with a graphite aluminum composite. So I think we have to really sit down and analyze very carefully just where we are and what is going to happen as far as these composite systems are concerned.

Now, I have tried very briefly and sketchily to concentrate on interface. Our next speaker, Dr. Kanuss, is going to talk about the continuum.

DR. MCCULLOUGH: Thank you very much.

The next speaker is Dr. Knauss.

DR. KNAUSS: The fact that I am intruding on your coffee time is a reminder to me that in twenty minutes one cannot really represent or present to an awake audience a research project that has extended over several years. Therefore, I have chosen not to speak on what I have done or what one can do, but rather try to point out three, essentially three problem areas that have to do with the problems that will face us in the future.

I would like to address the first one of the things by hooking up with a remark that John Halpin made this morning to the effect that most of us are trained in dealing with engineering problems on the basis of experience with metals. With metals, we do essentially the following: We determine their properties in laboratory tests, which are conducted over a period of a day, minutes, or so, in a testing machine. We use this data to design the structure. We calculate out the stresses in the structure, make use of these properties and then predict whether the structure holds up. If it doesn't, we beef it up in some way or redesign it.

That has worked quite well for us with metal structures except for problems where over long periods of time corrosion or fatigue has had its word.

When we come to polymers, reinforced polymers or non-reinforced ones, we tend to do the same thing today. We perform tests in the laboratory, which in most cases

when we are dealing with rather rigid polymers, extend over something like maybe a day or a week, and we measure the properties, apply them in calculations of the strength of the structure, and then hope that the measurements and the calculations we have performed will see the structure through its total lifetime.

The lifetime of such a structure, the one that we are faced with here, is usually on the order of several years, and let me just throw out for order of magnitude comparisons five, ten, or twenty years. We would like to have an airplane last that long.

So the problem we are faced with is that we do short term material characterization where it becomes feasible, economically feasible to do this. We cannot test material properties on a reasonably large scale for applications over ten years, because a structure is supposed to fly before then. We are therefore faced with extrapolating the short term data to long times on the order of ten to twenty years, and that turns out to be somewhat problematic, if we have data on the order of a week.

I'd like to connect to another remark that was made this morning by Max Waddoups.

So I don't misrepresent you, Max, it's quite laudable if we can make measurement properties or properties determinations to design a structure within a six-months to nine-months time space. But as far as I'm con-

cerned it seems to me that it's just about at that time that the fun begins, because we can then maybe design a structure, but we are not certain that the structure will really perform for the next ten, fifteen years as we hope it will.

I'd like to allude here to a reasonably well documented problem in the solid propellant missile area where just this kind of design approach was taken, something more than a decade ago, where missiles were designed, Minuteman is one of these, has gone through several revisions since then. One has designed these, they have flown successfully, but the problem that has recurred was overlooked in the beginning, not because nobody thought of it, simply because nobody knew really what to do about it at the time, was that the system was designed for 10 years or 5, and after the time was up the question arose, can we use the missiles longer than we had originally intended them for. Because this would save a tremendous amount of dollars.

And it was at this point that it was discovered that we really don't have the basic knowledge to make that decision at this time.

So if we design structures that fly on a two-three-year basis, that does not mean that we have the knowledge to predict ten years hence whether the system will perform satisfactorily over a longer period of time. And undoubtedly this question will come upon us.

That is only one problem against the background of which I would like to make my following remarks, because it seems to me that if we cannot test for long periods of time in order to make use of real time test data that we have to devise some kind of a predictive technique on the basis of which we can make judgment whether laboratory measurements are meaningful for long periods of time.

I have the belief that the failure of most structures, other than large deformation creep, is connected with the growth and propagation of cracks, and I would simply ask at this time that we accept this as a fact. After 15 minutes of my following presentation you may wish to discuss this, but for now let us assume that this is so.

Cracks may appear in all sizes, at all sorts of interfaces, small, large, compared to any other geometry of the solid, and I would like to submit that if we understand how these cracks grow as a function of time and possibly how they coalesce to make larger cracks we begin to understand the part of the failure process in these materials that we call polymers. And from a macroscopic viewpoint, I would like to refer to them as time-dependent materials.

Therefore, if we think of cracks as growing we think in terms of metals, metal-type structures, in terms of a question I'd ask, when does a crack begin to propagate? With polymers we rather have to modify this question and

ask not, when does it begin to propagate, but, really, how fast does it propagate? Because we will see that cracks tend to propagate under small loads but they may grow so slowly that for the life of the structure, even 10, 20 years, it may not be of any consequence for us.

So we have to ask the question, if the cracks grow, how fast do they grow, and how fast does the failure process begin to proliferate?

Let me first talk about a dry material, that is leaving out moisture and temperature for the moment, and let me turn to an idealized geometry which I show in the first slide. This is simply to indicate that we are talking about a crack regardless of the size of the crack as it finds itself in a composite structure, and what I'd like to illustrate here is simply the basic idea of what happens to a crack that is in a loaded structure. We think here of a structure that is loaded by a stress σ at infinity. That may be a function of time, and we may think of these forces being transmitted through the medium to the little bit of material at the tip of the crack, which is actually the material that upon crack propagation is the one that goes from an apparent continuum over into this continuum and thereby allows propagation of the crack.

And let us simply think of this little bit of material as being subjected to a very high state of stress. As a matter of fact, we may think of this whole structure

simply as a test machine which transmits the boundary forces to a little piece of test material at the tip of the crack. It is our misfortune that this test machine is rather flabby or elastic in contrast to a very rigid MTS machine, and in particular if we talk about a polymer it may not only be a very flabby test machine, it may be also one that depends on the time history by which we apply these forces. Because we have to think of the matrix of a polymer as being essentially time-dependent, exhibiting time-dependent properties, so that the forces transmitted through this little material depend on the history of load that we apply here through the time-dependent properties of the intervening material.

We may characterize possibly, and I only throw these out as some very simple parameters of a characterization process for the fracture here, we may think of this little piece of material as being able to sustain some kind of limiting stress, which the polymer physicists may look upon as the ultimate load-bearing capability of the polymer chains. Let me refer to that in later slides as Σ sub-zero when it appears. We may further think of this little piece of material when it gives way as having absorbed a certain amount of energy, which later on I should like to refer to as Γ as some kind of a characteristic quantity for this little piece of material.

I have said that the material, the bulk material here, may be viscoelastic, and I will try now to do the

almost impossible, and I ask your indulgence, to summarize half an hour's to an hour's discussion into three slides.

Now, I do this primarily or only for the purpose that when I get done with the three slides I haven't pulled something completely out of the air, to give you the feeling that there is some logic behind what I do, because at the end of the third slide I would like to refer to some quantities that allow me to partition the fracture propagation process into its essential basic parts which then allows us to make a statement as to where the geometry, where the material properties, possibly the environment, enters into the fracture process, and thus I would like to separate the fracture problem to these three parts.

Let me go to the next slide, and this is supposed to illustrate -- disregard these curves, they are the same ones here superimposed. These are curves for the creep compliance of the material, which is essentially the following data for those of you that are not familiar with visible elasticity. Take a uniaxial tensile rod, subject it to a constant load, and measure the therefrom resulting type dependent elongation, creep elongation, that is shown here as a function of time for a particular polymer that has distinguished itself from epoxies primarily at its glass transition temperature is considerably lower than that for the epoxy.

In particular, for epoxy type materials we would have to consider this portion to the right essentially for the creep behavior, and perhaps this suffices for now as an indication that we are dealing with a time-dependent material here, which property, I would like to remind you, this property occurs later in a somewhat mutilated form, and that is why I show the slide here so that later on we can recognize and I can refer to it.

Let me choose instead of the last slide this geometry, the sheet geometry on the load. Let me choose a particularly simple geometry for which I can make some simple calculations, that is shown in the next slide, and what I'd like to do is consider a strip of a viscoelastic material. This has some relevance to a bonding problem, which is a composite problem, as Dr. Patrick said. Let us not ask for the detailed correlation between what I do here and how it relates directly to the composite. I am interested in the time-dependent process of the failure, a specimen that has rigid rails on the top and bottom which can separate by ripping them in a test machine and submitting the specimen to a strain ϵ sub-infinity, which is measured here. I can perform a stress analysis, a viscoelastic stress analysis, for the crack as the crack propagates, and now I make the assumption that the crack propagates at a constant velocity, and once I have the stress analysis I can perform furthermore, or apply a failure

criterion, and these two ingredients should produce for me a relation between the rate with which the crack propagates, depending on how much strain I have put on the specimen.

This is kind of the simplest relation or the simplest situation in which I can relate a loading on a viscoelastic structure to the rate with which the crack or the failure process occurs.

In the next slide there will appear this quantity, also the width of the specimen, which I have given the notation B , and with that we can go to the next slide in which I will refer only to -- out of all the equations, only to this one. I have said if I can perform a viscoelastic stress analysis, which I can do, and apply a failure criterion, which is given here as the energy criterion, it turns out it doesn't make any difference whether I use this one as long as it's still on the right side of the board. If I do that, I arrive at an equation that relates the strain to the velocity of crack propagation, which I have denoted here by \dot{a} , for the simple geometry, and the only reason I show this here is not to impress you with all the equations I can write down, but what this equation does for me, it separates, it shows fairly clearly where in this simple viscoelastic crack propagation problem geometry enters the problem, and where the material properties, namely, the creep compliance, enters the problem and where the failure

properties, intrinsic failure properties of the material, enter the picture. And then perhaps, and I admit this is in a somewhat simplified way, and then perhaps we can ask how does the environment play a role in changing the various parameters that enter here. ΘR is really nothing but the creep compliance, that is an integral, which involves a creep compliance that's given here. So this represents the macroscopic properties of the -- the creep properties of the material, and in the argument of that function appears the stress, the cohesive stress that is the ultimate strength of the material that the crack tip can sustain, forget about the factor A^2 as for the unity. B here is the geometry, E infinity is the modulus.

Here again is the load that's applied to the structure, and in this particular case it's a constant. One can do this problem over again for time-dependent straining. There appears the energy Γ to which I alluded a little bit earlier as one of the material parameters that characterizes intrinsically the material. Here is again a material parameter, and B is the geometry.

So what this equation does for you is essentially, and you could do this for different geometry in a little bit better way, what it does essentially is separate the various aspects of the geometry, the material behavior, both with regard to its bulk and to gross behavior, and with respect

to the fracture characterization, fracture characterization being Γ and Σ_{∞} , it separates these, and we can then ask how does, for instance, moisture, how does temperature affect these various parameters?

Before I do that, let me show in the next slide what the result of this equation is. It's the solid line compared with the experimental points, and if we now ask what is the effect of, say, adding temperature to this picture, it says that if we know this much, and I do not have the time to detail this at great length, if we change the temperature to -- if we proceed to colder temperatures, then at the given strain this is log log plot, simply rules everything to its lower velocity, cold temperatures meaning slower crack propagation. If we speak about moisture, increasing moisture moves everything to a higher velocity.

There are two sources from which this effect can be gauged. One is simply that the creep compliance, just like the relaxation modulus, is directly affected by the moisture, as was pointed out this morning, and this afternoon, the change of the glass transition temperature is one of the ways in which this can be characterized.

But more important than that, it seems to me that it is right at this point where we begin to separate out from the macroscopic gross fracture process the intrinsic material parameters that characterize the fracture, namely, the surface energy Γ , this fracture energy, and Σ_0 ,

the cohesive strength of the material at the crack tip. Where the polymer physicist has a way of describing what should happen to these parameters if we change the molecular structure or if we put lubricants or diluants into the material, it is right here that I see the connection between the macroscopic structural application of the crack propagation process and the microscopic part that the polymer physicist can supply. And I have not seen much work done in this area, and perhaps this would be something that's rather fruitful.

Now, in these data you see embodied experiments that deal with steady state situations, namely, we prescribe a given strain or a given load and the crack will propagate at a constant velocity. It's one of the simplest ways in which we can do things, but it's very natural that we do this, and we do this more or less all the time in the laboratory, we choose the simple histories and subject material to them.

I would like to submit that only in particularly simple material cases are we allowed to make use of data such as this and extrapolate it to non-simple histories. In particular, I would have to ask if this was data for a general, an arbitrary viscoelastic solid, would I be justified in making use of this data and calculating from it in some way that I'm familiar with and you may not be; are you justified in applying this, for instance, to this cyclic

problem, where the load cycles periodically or not periodically? And one would have to answer to that question in general you are not.

We know some of the limitations under which this can be done, but for a number of materials that is not possible at all, and I do not have time to give you extensive illustrations for that right now.

Let me go to third point, having spoken briefly on this problem dealing with simple test histories, steady state crack propagation data versus load histories where cyclic or transient loads must be considered.

I have spoken here essentially of dry conditions and we now would like to ask what happens if we deal with a moist environment, and for that purpose, go to the next slide and refresh our memory or find out that the effect of moisture on so-called time-independent materials is not really new. What I have here is a data set on crack propagation in glass -- that isn't inorganic glass. I should be specific here in this audience. If we deal with glass in a near vacuum we find that the crack propagation rate, which is plotted here logarithmically on the vertical axis, gains a fracture parameter which is similar to the strain in the previous slide. It is essentially the square of the strain to the previous slide. We find that there is a very moderate dependence on the crack propagation rate, on the applied stress or strain. However, if we add to that

moisture, and I now have to beg your indulgence for not being able to quickly translate the number of grams per cubic meter of moisture in the air into relative humidity, but if we add to that moisture we see that these curves become strongly dependent on the velocity that has become strongly dependent on the applied load. And, therefore, for relatively small loads, you can already obtain crack propagation velocities in inorganic glass, whereas in dry conditions you do not.

The same thing can be observed in epoxies and the question that immediately arises, what is the source of this, and what does this observation have to do with a design problem such as we may be concerned with here? Again, here we deal with, in these examples, crack propagation under steady loading conditions, and if we ask what is the most likely reason why the crack propagation velocity is so strongly affected by the moisture content, one must submit that the material is -- the little piece of material at the tip of the crack is subjected to a higher stress, and because of a strong dilatation that occurs here the ingress has its direct effect on the cohesive properties or on the flow properties of the material, and therefore one should expect once the viscosity is decreased of the material locally one should expect an increase in crack propagation or an increase in the failure process at the crack tip.

The next question that one must ask then is, is this true regardless of whether the material is soaked with mois-

ture or it is dry, is put into a moist environment and then loaded? But what I am again referring to here is the question of whether the test data procured in this particular fashion is also indicative of what happens under transient conditions. And the answer is not immediately obvious, but we need to remind ourselves only that we are dealing here with phenomena that have potentially different time scales. There is a crack propagation history and as the crack tip material becomes available to moisture ingress from the outside due to the rate of crack propagation, a certain amount of time is necessary for the moisture to ingress into this highly strained region. And as Dr. Francis referred to a little bit earlier, this problem cannot be separated, it seems to me, intrinsically from the question of coupling between the state of strain and the crack tip, the rate of moisture ingression, and the temperature as well.

So again here we are faced, if we want to understand the problem of what an airplane is going to see in its entire lifetime, we have to become familiar with a question of how does a crack react under a varying load history when it sees also a varying moisture history. And these are then some of the problems that I see coming towards us.

And let me in conclusion summarize them briefly by one sentence once more. We have to be concerned with the problem of having short time test data which needs to be

extrapolated via some refined knowledge to long term, say 10, 20 year predictions. We have to be concerned with problems in the laboratory which deal essentially with steady state or simple load histories and how these are to be extrapolated to more complicated load or deformation histories. And, finally, we have to be concerned with the interphase that exists between the structural engineer who concerns himself with the crack propagation problem and the material scientist who knows what happens at the molecular scale and how these phenomena affect the material parameters with which the structural engineer has to be concerned in the fracture problem.

With that, I should like to thank you for your attention.

[Recess]

4. Test Methods and Experimental Research

DR. MC CULLOUGH: We will continue our discussions with the topic, Test Methods and Experimental Research. There has been a slight change in speakers. Jack Reynolds of General Dynamics will give the first paper rather than Lee McKague.

MR. REYNOLDS: In testing graphite epoxy materials the most serious problem encountered in environmental stimulation is the moisture absorptive properties of the material itself. Moisture diffuses into epoxies at a very slow rate.

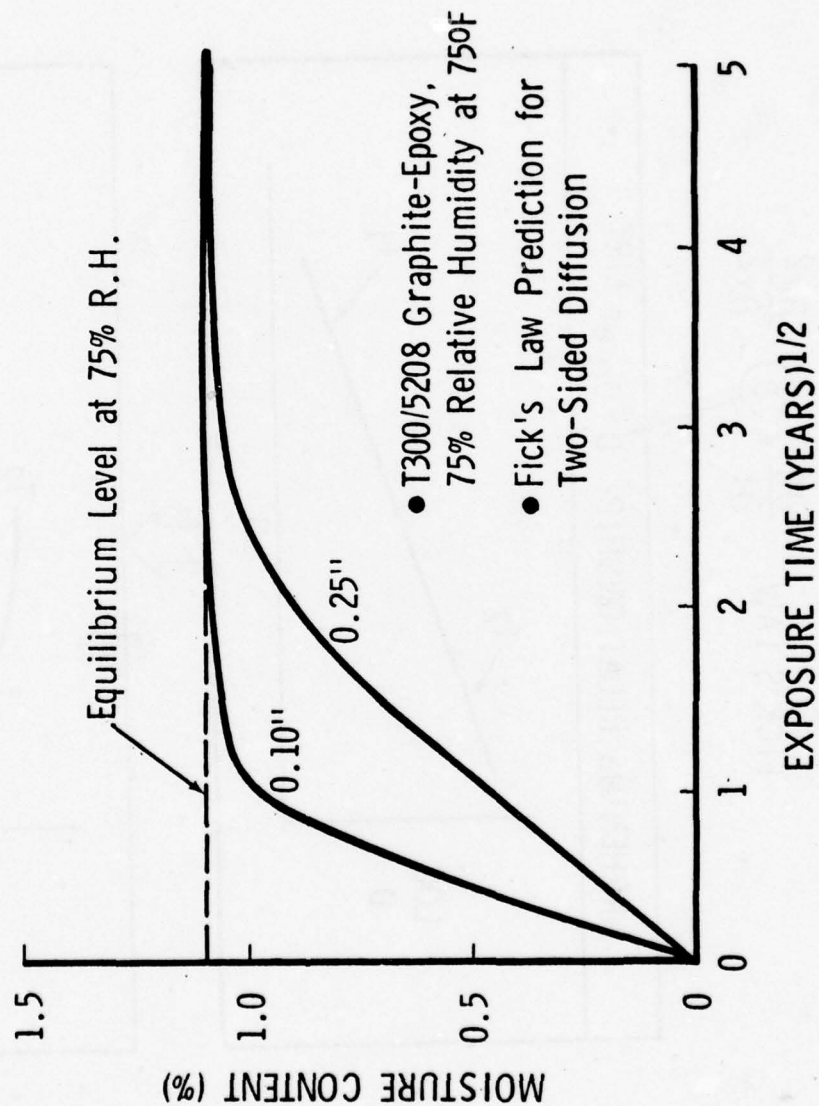
First slide, please (R-1).

Here we see the equilibrium moisture level at 75 per cent relative humidity saturation. This is a fairly typical runway condition. With a quarter-inch thick laminate we see that it reaches equilibrium in about 15 to 16 years, which is the service life of some vehicles. If the panel is thinner, more like a tenth of an inch, we reach equilibrium in maybe four years, and if, indeed, only one side of this quarter-inch panel is exposed, it takes twice as long to reach an equilibrium. So it is very, very slow process. These curves are based on Ficke's law, two-sided diffusion.

Next slide, please (R-2).

So it's the duty of the laboratory to find ways to accelerate this process. The only mechanism we have for accelerating moisture absorption is through increased temperature. Based on Ficke's law and Arrhenius' relationship, we see that the log

DIFFUSION IS A SLOW PROCESS

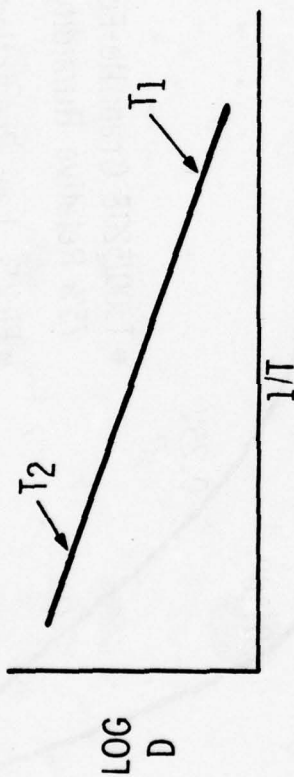


R-1

ACCELERATION REQUIRES TEMPERATURE

FICK'S LAW: $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$

ARRHENIUS RELATIONSHIP: $D = D_0 e^{-E/RT}$



R-2

of the diffusion coefficient when plotted against the inverse of temperature gives a line like this with T_1 being runway or room temperature conditions, T_2 being an accelerating temperature. This plot gives us the relationship of per cent moisture versus the square root of time.

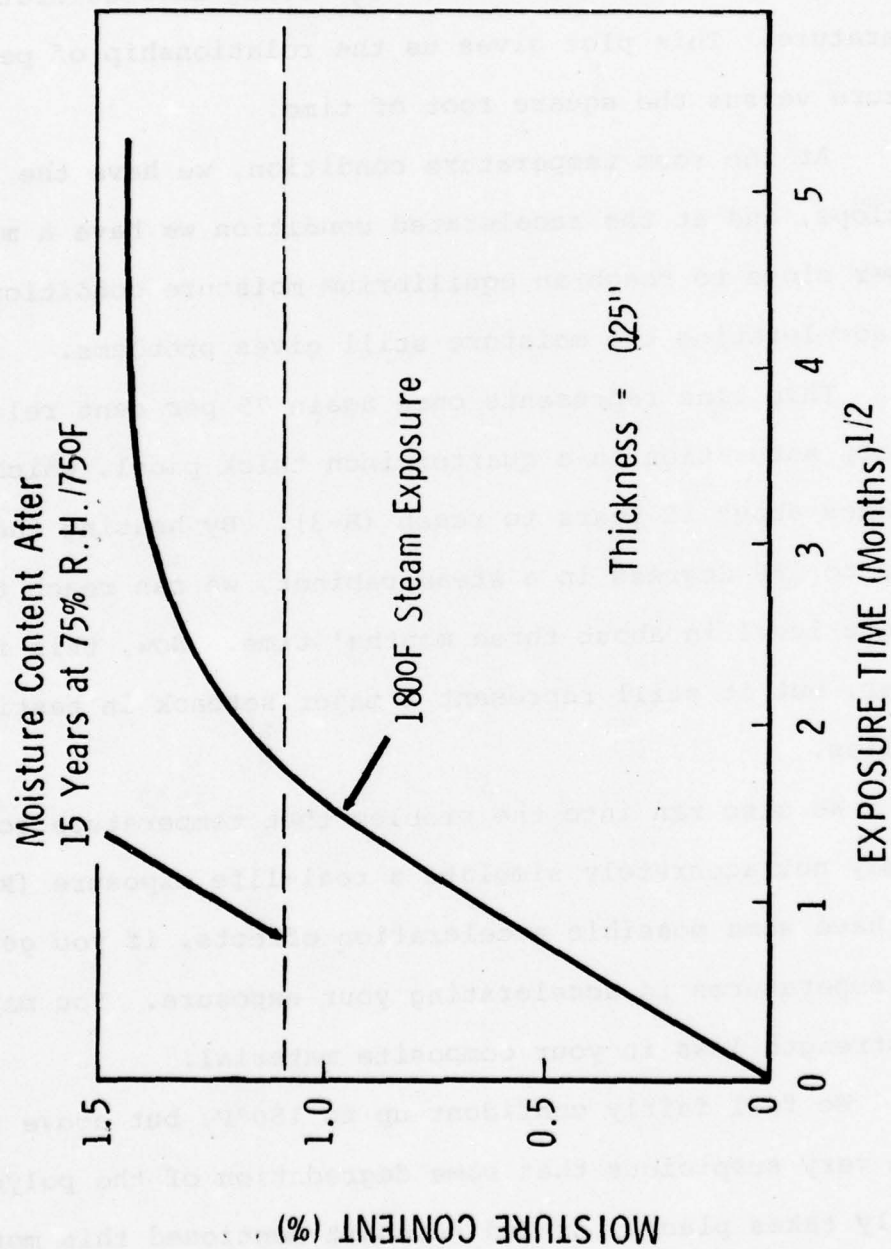
At the room temperature condition, we have the long low slope, and at the accelerated condition we have a much steeper slope to reach an equilibrium moisture condition. But even accelerating the moisture still gives problems.

This line represents once again 75 per cent relative humidity saturation in a quarter-inch thick panel, which we saw takes about 15 years to reach (R-3). By heating the specimen up to 180 degrees in a steam cabinet, we can reach the same moisture level in about three months' time. Now, this is much quicker, but it still represent a major setback in testing schedules.

We also ran into the problem that temperature acceleration may not accurately simulate a real-life exposure (R-4). You'd have some possible acceleration effects, if you get to high temperatures in accelerating your exposure. You may have some strength loss in your composite material.

We feel fairly confident up to 180°F, but above that we are very suspicious that some degradation of the polymer actually takes place. As Ted Reinhart mentioned this morning, accelerated moisture doesn't actually simulate the distribution profile found in a realistic real-life exposure. Plotting

ACCELERATION MAY REQUIRE MONTHS OF EXPOSURE



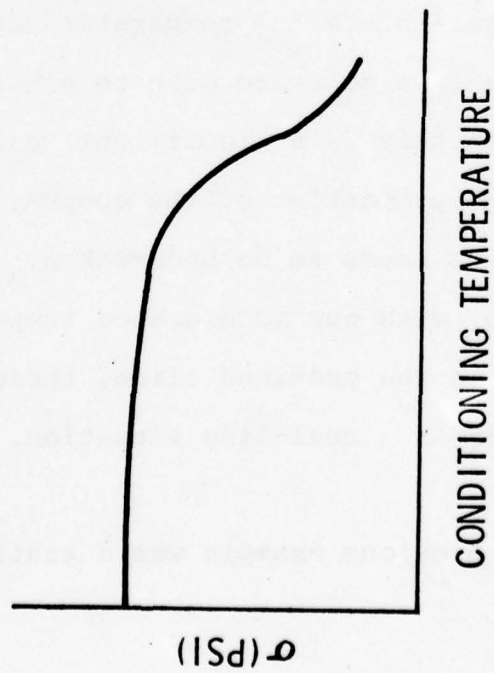
R-3

314

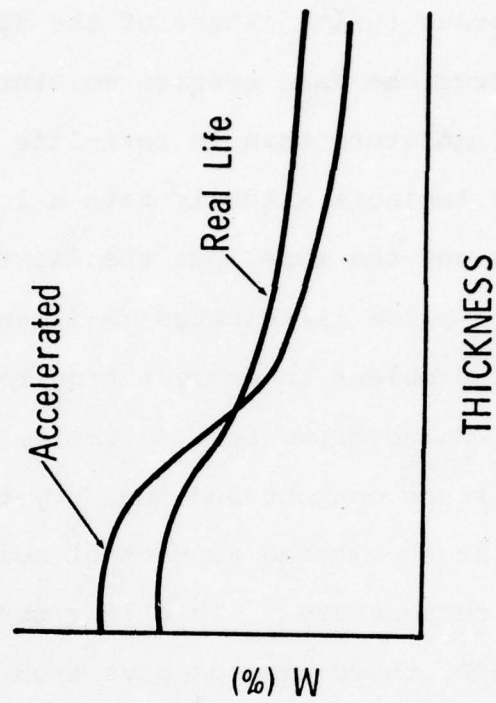
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25 Mar '76

ACCELERATION MAY NOT ACCURATELY SIMULATE REAL LIFE

• POSSIBLE ACCELERATION EFFECTS



• DISTRIBUTION VARIATIONS



R-4

moisture versus the thickness of the specimen, accelerated exposure gives the same average moisture content, but edge plys have higher moisture than in real-life exposures and the center plys of the laminate actually have a lower moisture content. It averages out the same, but the distribution is different.

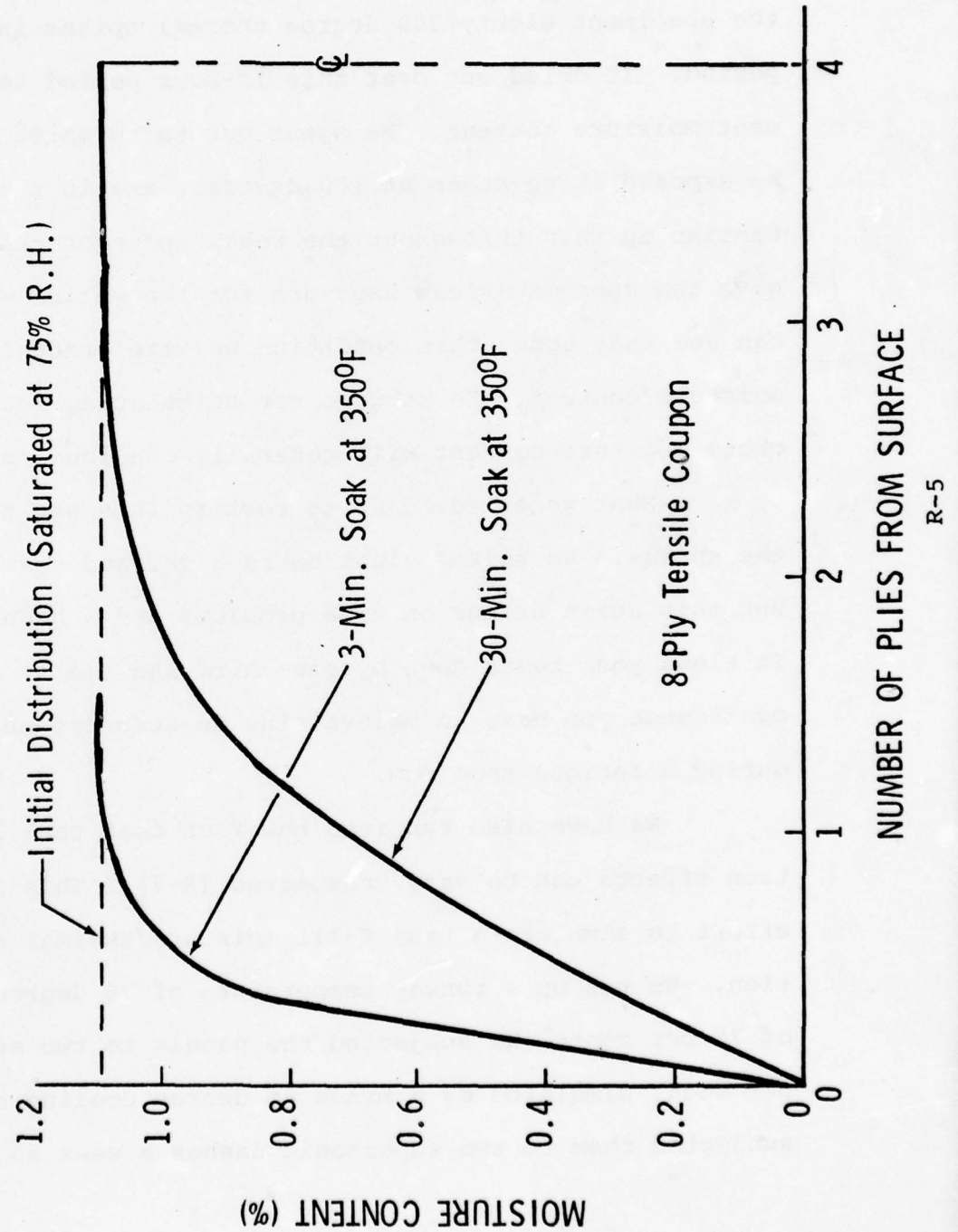
This slide illustrates (R-5) another problem that gives us a lot of problems in coordinating results from different laboratories. Whenever we take a sample, and initially soak it to a given moisture content and then try to test it at some elevated temperature varying amounts of moisture are lost, depending on time at temperature. This line represents a three-minute soak at 350°F, these are the plys from a surface. You see the surface-most plys fairly well dried out, but these reabsorb rather quickly and do not represent a very large per cent weight loss. However, if you leave the specimen in your test fixture trying to equilibrate the temperature for 30 minutes, you see that we have lost moisture down to even the third ply, and in a thin specimen this is a significant weight loss and has a large effect on the properties of the coupon. Some effect to standardize soak times needs to be undertaken.

Also, with our accelerated temperature profile, as we pointed out in the previous slide, these outer plys have more moisture than in a real-life situation, thus magnifying this effect.

The previous example was a static type exposure situation

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SPECIMENS DRY OUT DURING HOT TESTS

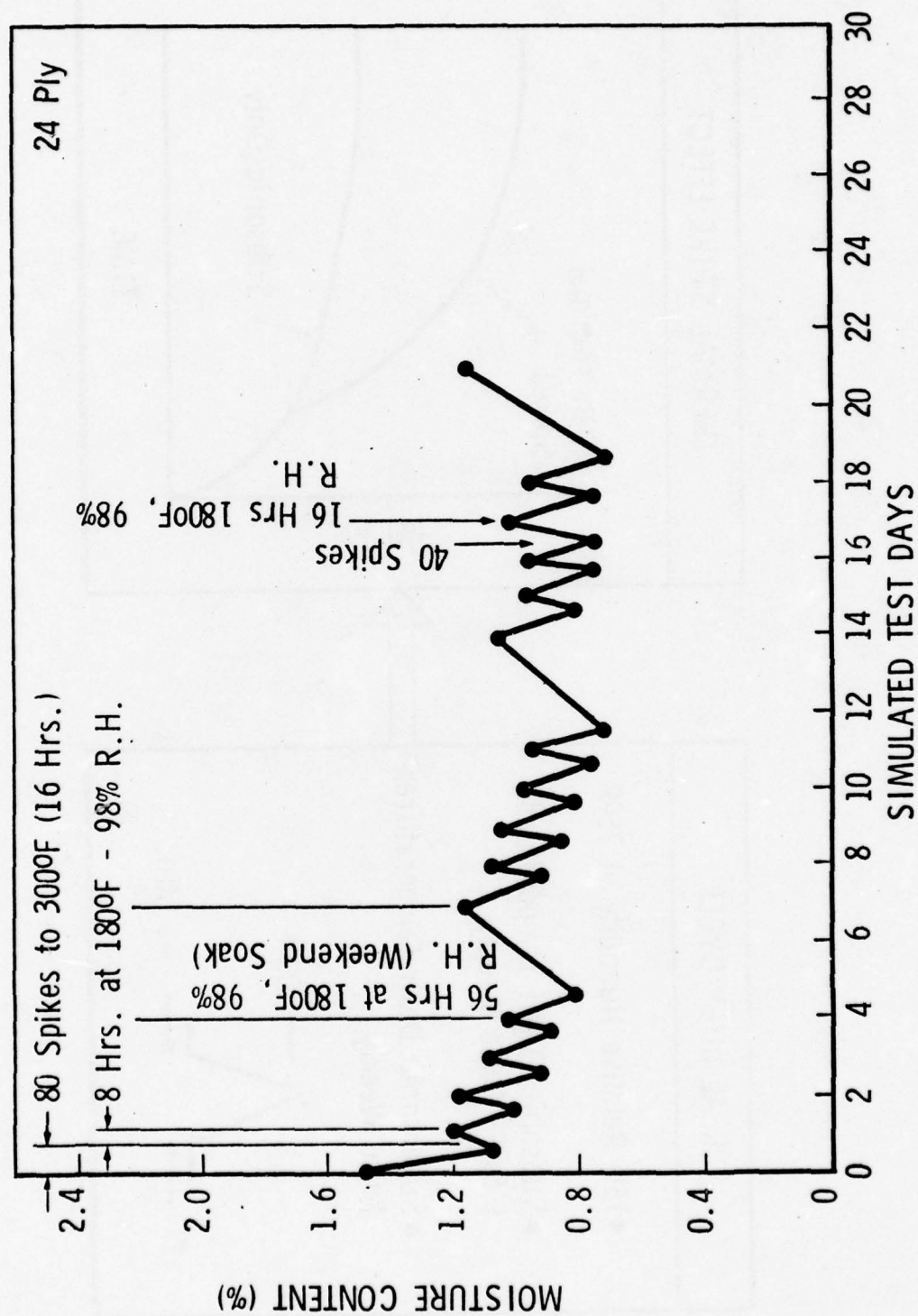


Here (R-6) we have a fatigue type situation of some dynamic test spectra that's applied to a composite material, saturated to a predetermined moisture level, and then going into cyclic fatigue at high temperature. In this particular case, we were giving the specimens eighty 300 degree thermal spikes in a 15-hour period. It dried out over this 15-hour period to around one per cent moisture content. We spent our third shift resoaking it. We exposed it to steam at 180 degrees, and it recovered part way. Continuing this throughout the week, and over the weekend we gave the specimen steam exposure for the entire weekend. You can see that under this condition we were gradually losing our moisture content. So we were not stimulating real life exposure where moisture content will generally continue to increase.

What we tried to do to rectify this was to cut down on the spikes. We spiked eight hours a day and soaked sixteen. But this again brings on time problems and scheduling problems. It slows your tests down by one-third and really messes up the confidence you have in maintaining an accurate moisture level during a fatigue spectrum.

We have also run into the fact that real life simulation effects can be very unexpected (R-7). This slide shows an effort to simulate a true F-111 moisture/thermal exposure situation. We set up a runway temperature of 76 degrees and a humidity of 75 per cent. We subjected the panels to two subsonic flights per week, simulated by a minus 65 degree cooling cycle and we subjected them to two supersonic dashes a week as shown in this

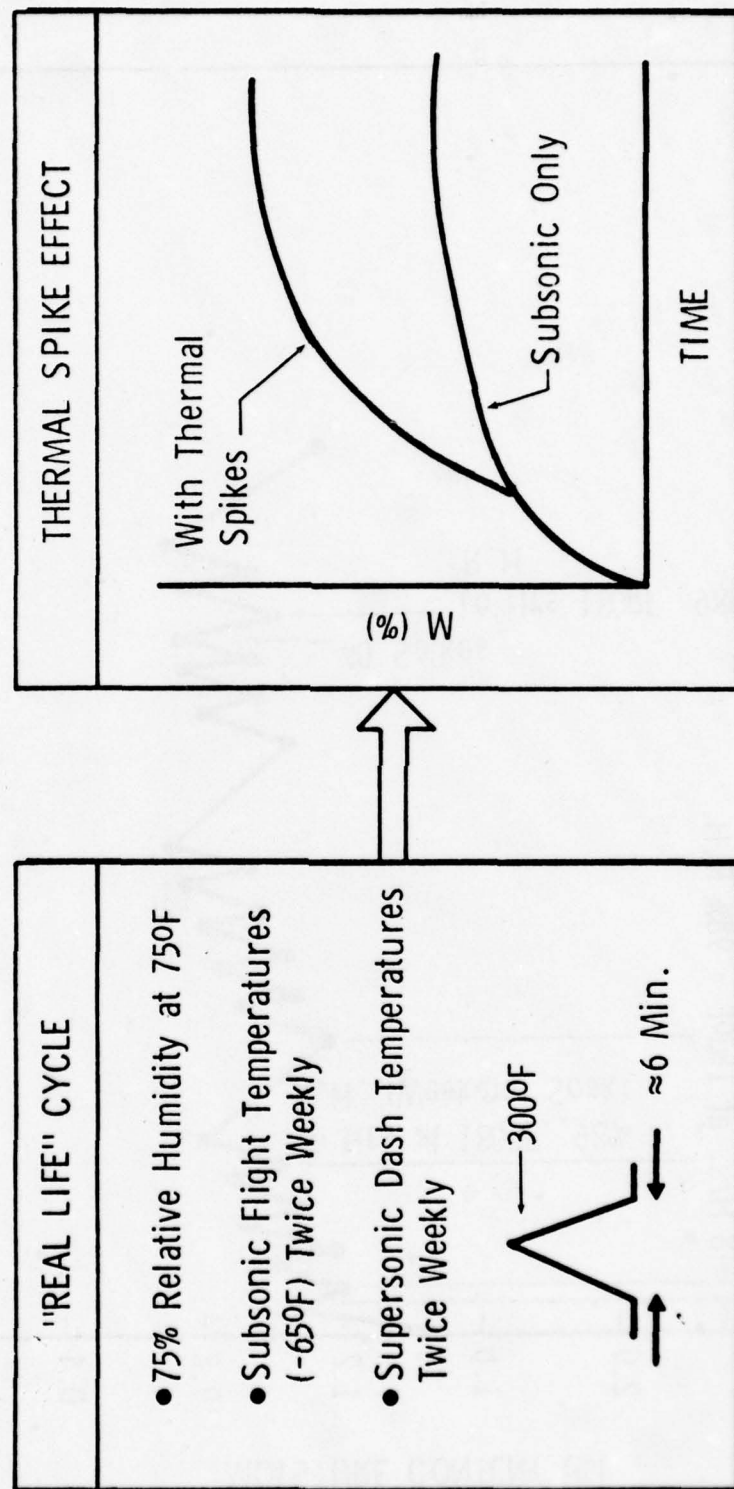
HOT FATIGUE TESTS NEED "RUNWAY TIME"



R-6

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23 MAR '76

REAL LIFE EFFECTS CAN BE UNEXPECTED



R-7

temperature profile. Over a six-minute period, we increased the surface temperature to 300 degrees and cooled it back down to room temperature. We had some specimens that only saw the humidity. Some saw the humidity in the subsonic, some saw all three. The effect we got, Ted Reinhart mentioned this morning. We see our normal saturation curve of the runway conditions and of the runway conditions plus the subsonic flight. The specimen saturates just as you'd expect in 75 per cent relative humidity. But, when we begin to apply the thermal spike at a certain moisture threshold we experience this wild excursion of moisture absorption, and as Ted pointed out, you can dry this moisture out but it does not come back to the original absorption curve. It immediately recovers to this higher absorption level.

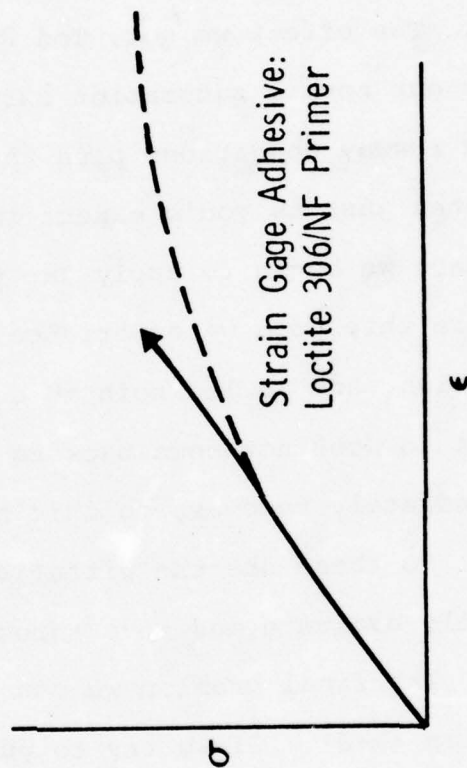
So these are the pitfalls you can experience. You must carefully evaluate and move through these "real life situations".

The final problem we run into is in data gathering and reduction (R-8). If we try to put strain gauges on composite tensile coupons or beam specimens, we have had all sorts of problems. We put the gauges on before conditioning and we run into gauge failures. We have tried different adhesives, we have tried overcoats with RTV rubber, but when we put them into moisture conditioning, if we don't have an adhesive failure we have decomposition of the strain gauge itself. We have had up to 10 ohm resistance changes just from wetting the strain gauges in the environments.

We have tried two methods of rectifying this. First we have presaturated our specimens to a known moisture level. Then

DATA REDUCTION IS A PROBLEM

- GAGING BEFORE CONDITIONING → GAGE FAILURES
- GAGING AFTER CONDITIONING:
 - HEAT CURING ADHESIVES → DE-CONDITIONING
 - ANAEROBIC ADHESIVES → LIMITED STRAIN LEVELS @ TEMP



R-8

we put on our strain gauges and cured them as short a time as possible and then reexposed the strain gauge specimens for a very short period to bring the moisture level back up to where it previously was. We can get away with doing this because they're not exposed long enough to damage the gauges or the adhesive.

The other method we have tried is the use of an anaerobic adhesives, which I understand the Air Force has had considerable success with. These are polyester type adhesives which cure at room temperature and will cure in a high humidity environment. This seemed like an ideal solution, but we found that while they do follow the stress strain curve very nicely up to about 2,000 microinches strain and about 265 degrees Fahrenheit, when you try to go to the upper regions, say 10,000 microinches, plus 350 degrees, we appear to get some kind of adhesive slippage. It gives us bad data. We are not quite sure why yet.

Presently, any time we are having to go to a high strain level or to high temperatures, we are having to go back to this heat curing adhesive.

In conclusion, we have done a lot of experimentation with the moisture problem, and about the only advice we can give is that you must allow for it in any scheduling you do. It's very treacherous when trying to plan ahead.

DR. MC CULLOUGH: Thank you very much.

The next speaker is Professor Karasz from The University of Massachusetts.

DR. KARASZ: Thank you very much, Dr. McCullough.

I want to talk about the interaction of polymers with water from a very basic molecular level, and I want to introduce terms which apparently have not been used here yet - principally involving the concept of bound versus free water. If we think of a solution of a polymer in a solvent, water in this particular case, and compare this with a homogeneous mixture of water in a solvent, I think it is fairly apparent that in the former case there is a gross heterogeneity in the concentration of the macromolecule as a function of distance through the solution. This effect has been studied by a wide variety of investigators including those interested in biopolymers and in synthetic molecules, and there has been a large amount of data generated. I want to try to bring some of it together in an effort to apply the problem that we are considering here.

In Fig. 1 are presented some of the various experimental techniques that have been applied to this problem and I have divided them into kinetic and the thermodynamic techniques. In this paper I want however to concentrate on the latter.

The kinetic techniques, here defined as those involving rate processes include a wide variety of diffusion

INTERACTION OF BULK MACROMOLECULES

WITH WATER

EXPERIMENTAL TECHNIQUES:

1. KINETIC:
 - a. DIFFUSION (TRANSLATIONAL, ROTATIONAL, SELF)
FROM E.G. NMR (T_1 = SPIN-LATTICE; T_2 \equiv SPIN-SPIN RELAXATION); DIELECTRIC RELAXATION.
 - b. IR, RAMAN SPECTROSCOPY.
 - c. NMR (SHIFTS)
 - d. LOW ANGLE X-RAY, ETC.
2. THERMODYNAMIC
 - a. ADSORPTION PHENOMENA.
 - b. THERMAL METHODS: CALORIMETRY (C_p , ΔH , ETC);
THERMAL EXPANSION.

CONCLUSION:

IN HYDROPHILIC SYSTEMS 10-40 WEIGHT % WATER IS "BOUND" \equiv
"UNFREEZABLE"

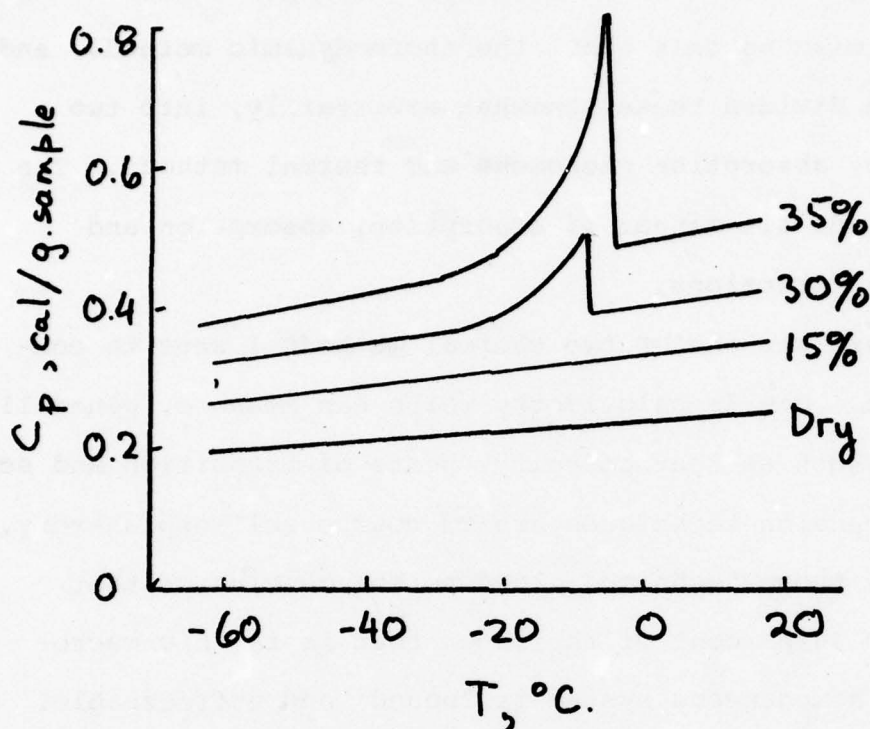
FIGURE 1

techniques, both of the kind in which the water diffuses into the polymer, which we have heard about before, and the symmetrical situation where the polymer diffuses into the water. Shown in Fig. 1 is a selection of some of the many techniques, some of them extremely sophisticated, which have been employed.

In general these diffusion techniques, the infrared and Raman spectroscopic techniques, take cognizance of the fact that the macromolecules soluble or insoluble, have surrounding them a so-called hydration shell, which is believed to be a shell of water that is more tightly bound to the macromolecule than in the bulk system. Thus there is a gradient from a macromolecule to the bulk system involving layers of bound water and free water, but, of course, to divide this into two sections is an artifact, there is in fact a continuum in any measured property.

Now, the other point that I want to make is that even in a system in which bulk water is present, it may be present in extremely small globules, of micron or submicron dimension. Thus it is possible that the properties of even this "bulk" water do not correspond to the properties of water, in a beaker, because of thermodynamic interaction on the one hand and because of Laplace's equation on the other.

These kinds of measurements have yielded, in some cases, a great deal of information concerning the hydration



1. KERATIN-WATER
 [(Haly and Smith,
 Biopolymers 7,
 459 (1969)]

2. FOR PET: 1.3 Wt.% absorbed; 0.6% freezes.

3. Schematic of system with $T_g < 0^\circ\text{C}$.

Measurable parameters:

\bar{C}_{pi} , ΔH_f ,
 $\Delta \bar{T}_g$, $\Delta(\Delta C_p)$

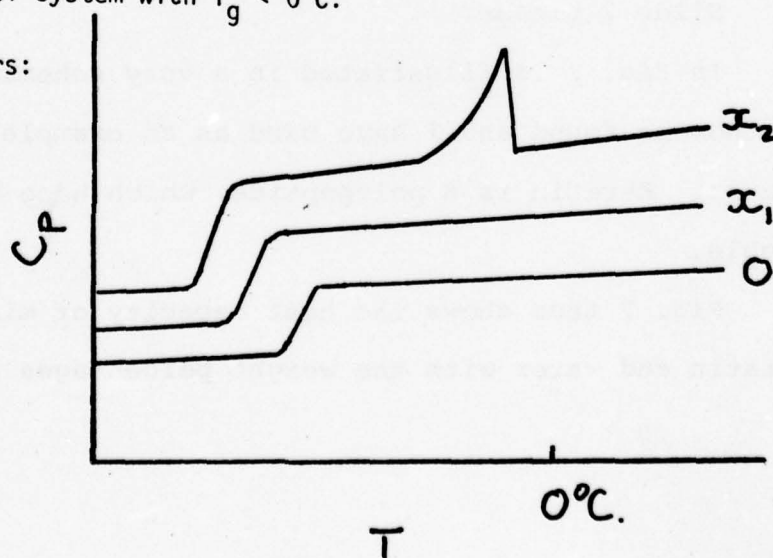


FIGURE 2

shell, though I do not wish to pursue this point here. Instead, I wish to talk about the thermodynamic methods, and here I have divided these somewhat arbitrarily, into two categories: absorption phenomena and thermal methods. The former include all manner of adsorption, absorption and solvation interactions.

There are one or two thermal methods I want to concentrate on. One is calorimetry which can measure, generally, properties such as heat capacity, heats of transition and so forth. Thermal expansion techniques are of course self-explanatory.

All these techniques lead to the conclusion that about 10 to 40 percent of the water that is in this macroscopically homogeneous system is "bound" and unfreezeable. That is if you take the system down below 0°C, one will find that this 10 to 40 percent water does not freeze in the same manner that bulk water does. This fraction of course depends on the chemical structure of the macromolecule and on its relative hydrophilicity.

Slide 2 please.

In Fig. 2 is illustrated in a very schematic way the phenomena found and I have used as an example keratin and water. Keratin is a polypeptide, which happens to be insoluble.

Fig. 2 thus shows the heat capacity of mixtures of keratin and water with the weight percentages of the

latter as shown. This incidentally is an apparently homogeneous system, with of course no free water.

The measurement of C_p of the dry polypeptide is shown in the bottom curve; it increases slightly with T as is characteristic of polymers. Even if one adds 15 percent of water there is no essential structure to the measured curve. The heat capacity, (per gram of sample) is higher because of course water has a relatively high heat capacity. When one adds perhaps 30 percent water one sees a small fusion peak. The characteristics of this are as follows:

- 1) typically the amount of water as measured by the heat of fusion, (from the area under the peak) is substantially less than what one would expect from the weight of added water.

- 2) the maximum melting point is depressed typically by a few degrees from zero, and

- 3) there is a broadening of the melting endotherm.

As more water is added, the fusion peak increases in area and may move or may show some secondary structure. This was shown by A. Haly (C.S.I.R.O., Sydney, Australia). The dry keratin incidentally shows no transitions of any kind. It is at least partly crystalline, but one cannot get to the crystal melting point because of degradation. It does not show a glass transition, and there is some debate in the biopolymer community whether there is in fact a glass transition in these materials or not.

In contrast, what occurs in an essentially hydrophobic system, such as polyethylene terephthalate. This is a non-crosslinked soluble thermoplastic, whose chemical structure would indicate considerable hydrophobicity and consequently the equilibrium amount of water absorbed would tend to be rather small. It is, in fact, of the perhaps order of one or two percent. But even here Haly has shown that only 0.6 percent, or about 50 percent of the total amount of water that can be absorbed, freezes. This indicates again that even for relatively small amounts there is a distribution of water in the vicinity of this macromolecular chain, into freezeable and nonfreezeable material.

As a consequence of such studies, several questions arise. What is the state of the non-freezeable water? What is the state of the freezeable water? Are the properties of the latter the same as those of bulk water?

It should be added that there is some uncertainty and debate regarding the heat of fusion (80 cal. g^{-1} for bulk ice) of the freezeable water. However, it is possible to make measurements of the partial molar heat capacity of the relevant material with and without water present, and from this data deduce heats of fusion.

Let me return to the question of the state of the non-freezeable water, the water that presumably interacts so much with the macromolecules that when it is cooled to -100 or -200°C , it won't freeze. Can the water thus be regarded as amorphous?

In the literature one comes across a great deal of confusion with regard to this point. Not infrequently are encountered phrases such as "vitreous ice" which to me is a contradiction in terms. In this regard, it has occurred to us that if we take a polymer which has a glass transition temperature below 0°C , there is an additional parameter that one can investigate with regard to this point.

For example, in the bottom of Fig. 2 are shown schematic C_p curves for an amorphous polymer which has a glass transition below 0°C . If one measures the heat capacity as a function of temperature, the glass transition will appear as a discontinuity in the heat capacity. If one then adds an increasing amount of water, shall we say weight fractions X_1 or X_2 , one can visualize that the following sequence of events will take place.

First of all, one can expect that there is an amount X_1 which corresponds to a situation in which no freezing takes place, and therefore for which no heat of fusion is observed on reheating. On the other hand, this water may plasticize the glassy polymer. In this case the glass transition temperature is lowered so the phenomenon that is observed is an absence of fusion but a lowering of the T_g , plus some change in the magnitude of ΔC_p . As a zeroth order approximation, ΔC_p , the size of the discontinuity in C_p at T_g , is the arithmetically averaged sum of the ΔC_p 's for the water and the polymer. (Water of course has a glass transition). As one adds increasing weight fractions of water,

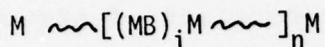
one would then expect to see then a further lowering of the T_g with again some changes in ΔC_p , plus eventually the appearance of a heat of fusion peak as for example curve x_2 in the bottom of Fig. 2.

So we have now a larger number of experimentally accessible parameters. These include partial molar heat capacities of the two components, the heat of fusion of the water, the change in glass transition temperature, and, finally, the change in ΔC_p .

There is thus a considerable amount of information to be gained from looking at such systems.

In Fig. 3 is shown the chemical structure of a polymer forming a very useful model in this context. The system that we have looked at is one that actually originated in Dr. G. Thomas' lab at the Army Materials and Mechanics Research Center, Watertown, Mass. It is a segmented polyurethane, block copolymer consisting of hard segments (where T_g is above room temperature) and soft segments, having a sub-ambient T_g . Segmented polyurethanes can form thermoplastic elastomers, because the hard segments segregate and/or crystallize, and therefore hold the material together, while the soft segments impart an entropic elasticity to the system at normal ambient temperatures. So we have got essentially a molecular composite consisting of a rubber matrix, the soft segmental material studded within it, the hard regions, perhaps a few tens of angstroms in extent.

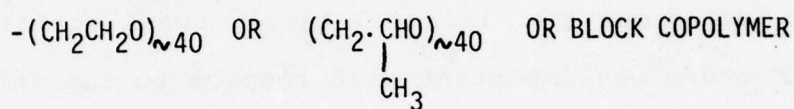
SEGMENTED POLYURETHANES:



M = 4,4'-METHYLENE DIPHENYL DIISOCYANATE (MDI)

B = 1,4-BUTANEDIOL

~ SOFT SEGMENT



CODE	MDI	:	B	:	~	
10PE33	4	:	3	:	1	100% PEO
5PE33	4	:	3	:	1	50/50% PEO/PP0
OPE33	4	:	3	:	1	100% PP0
5PE28	3	:	2	:	1	} 50/50% PEO/PP0
5PE33	4	:	3	:	1	
5PE40	6	:	5	:	1	

FIGURE 3
STRUCTURE OF SEGMENTED POLYURETHANES USED

There is a wide latitude of possible structures that can be synthesized relatively easily and it has therefore been possible to make a rather complete investigation of the effect of chemical structure on these materials on their interaction with water, for example.

In our system the soft block consists of structures of about 2000 MW ranging from polyethylene oxide, PEO, on the one hand, to polypropylene oxide (PPO) on the other. It turned out that this relatively small variation in chemical structure was important with respect to the interaction of the polymer with water. The reason is of course that PEO is extremely hydrophilic while PPO is relatively hydrophobic.

This effect of structure on water uptake is illustrated in Fig. 4 which shows the equilibrium water uptake as a function of structure and as a function of temperature. The lowest curve is for a polymer whose soft segment is all PPO, polypropylene oxide, while the highest curve is for a polymer containing only PEO. The intermediate structure, 5PE33, contains a block copolymer of equal fractions PEO and PPO. (Note change in scale on ordinate). These are all solids, of course, at room temperature, and will thus absorb water, more or less depending on the structure, and thereby forming what would be superficially considered to be homogeneous solutions of water in the polymer.

The PEO soft segment has a negative heat of solution, incidentally, so the amount of water absorbed goes up as the temperature goes down in the range of 0°C to perhaps 50 or 60°C.

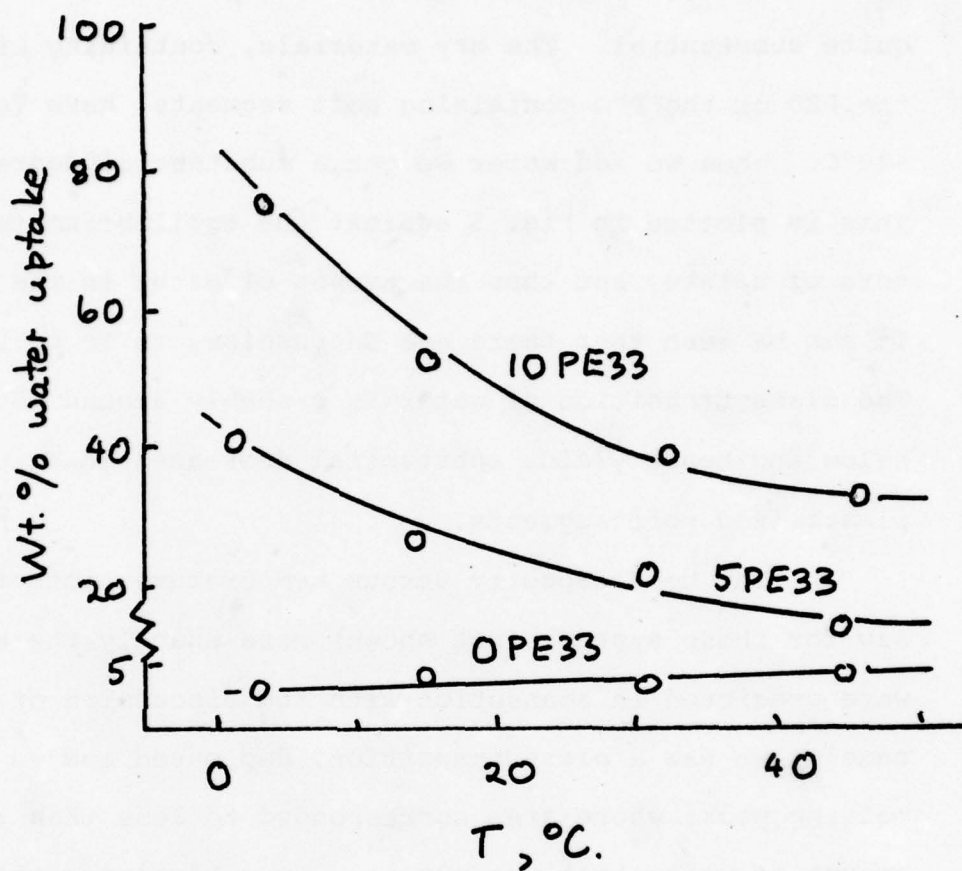


FIGURE 4

WATER UPTAKE AS FUNCTION OF
STRUCTURE AND EQUILIBRATION TEMPERATURE

The T_g behavior is shown on Fig. 5. The effect is quite substantial. The dry materials, containing either the PEO or the PPO-containing soft segments, have T_g 's about -40°C . When we add water we get a substantial decrease. This is plotted in Fig. 5 against the equilibrium temperature of uptake, and thus the amount of water in the system. It can be seen that there are depressions in T_g up to 30°C . The glass transition of water is probably around 150°K or below and hence yields substantial decreases in T_g of these plasticized soft segments.

The heat capacity versus temperature plots that we saw for these systems (not shown) were exactly the kind that were predicted in connection with the discussion of Fig. 2, namely, we saw a glass transition, depressed and we saw a melting peak, where area corresponded to less than the amount of water that was put in. By subtracting the amount of water represented by the area of the peak from the total amount that was added, we have a measure of the unfreezeable water. If we plot the amount of unfreezeable water as a function of the change of the glass transition temperature relative to the dry material, we get the almost straight lines shown in Fig. 6. On this I also show (dashed line) a theoretical curve calculated on the basis of a very simple equation representing the change in glass transition as a function of diluent content. The agreement is fairly good. One further point to discuss is the slight increase in T_g

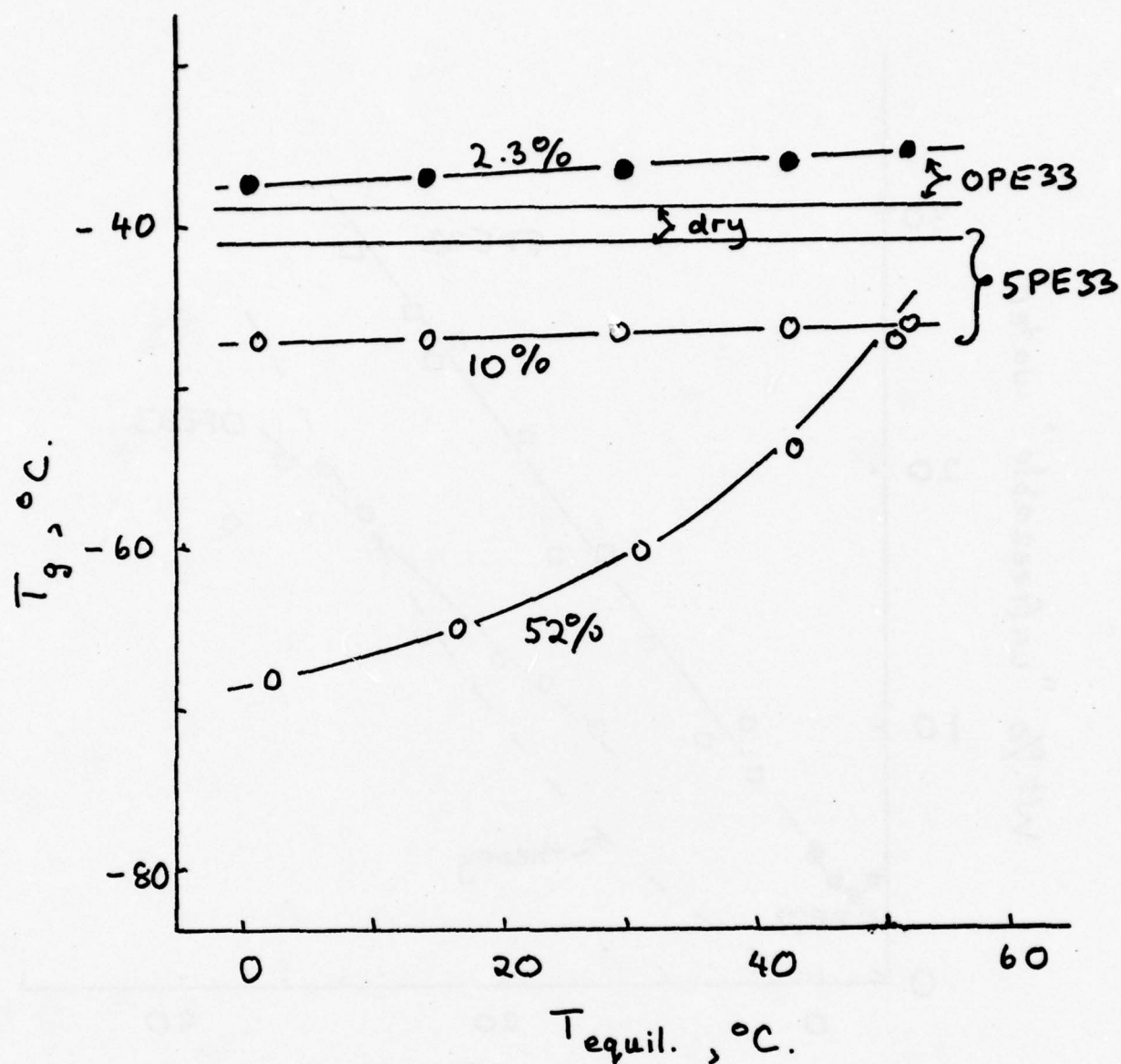


FIGURE 5

GLASS TRANSITION OF POLYURETHANE SAMPLES AS
FUNCTION OF ADDED WATER, EQUILIBRATION
TEMPERATURE AND STRUCTURE

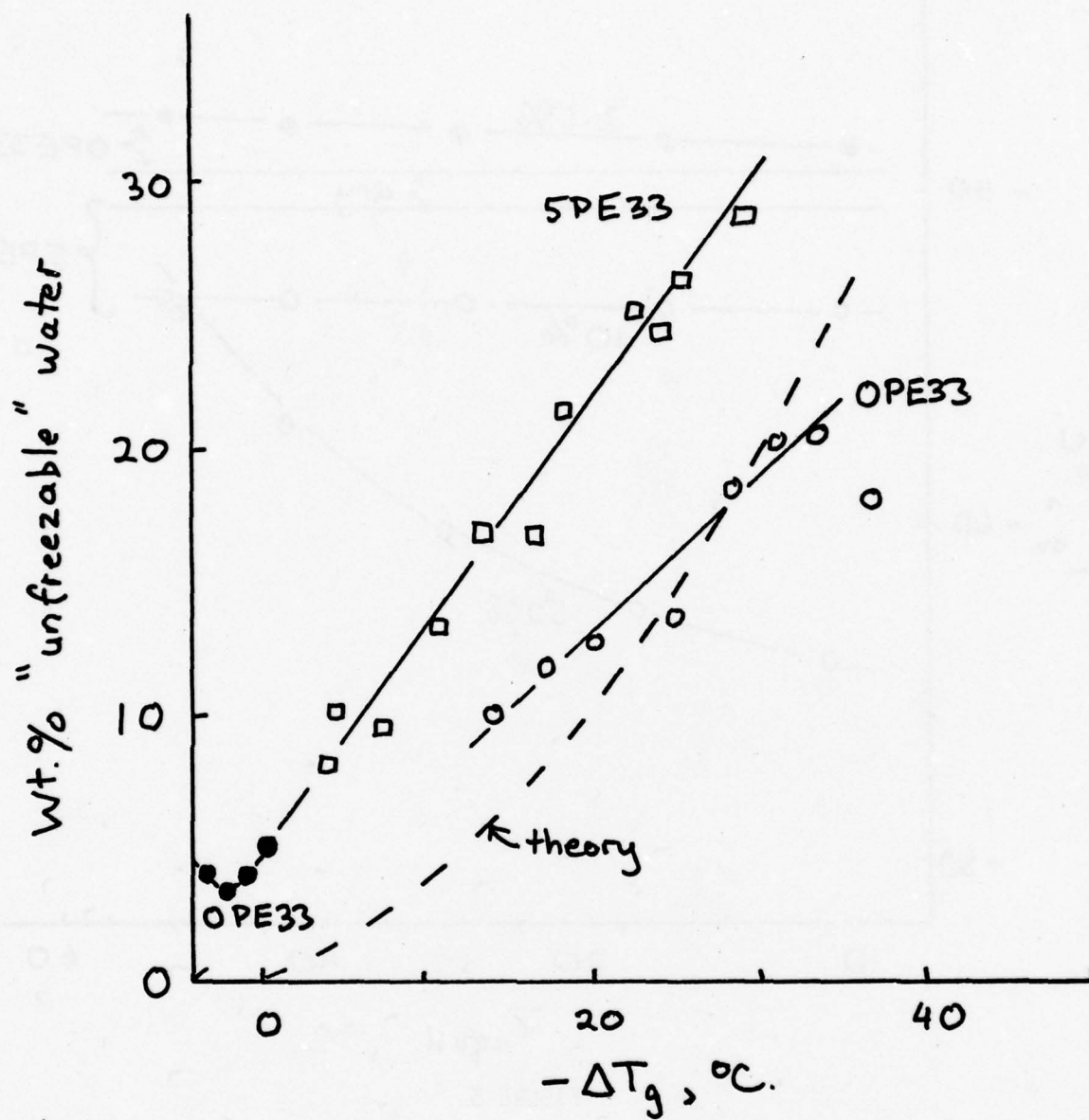


FIGURE 6

UNFREEZABLE WATER vs. T_g LOWERING AS
FUNCTION OF STRUCTURE

at low water absorptions. This is an antiplasticization effect, well known in other polymers. We may speculate here that this increase in T_g may be caused by an actual stiffening of the chain by adsorped water. In summary, we see several phenomena, but, importantly, no new concepts have to be invoked to explain the interaction of water with these polymers, except the notion that water has to be divided into freezeable, non-bound, and a non-freezeable, bound categories.

In Fig. 7, I have listed a number of conclusions. I have made these points separately, let me now make them together. There is a distribution of water into freezeable or unfreezeable portions as in our system. An interesting correlary is that if one adds a given amount of water, there is always a distribution. In other words, the adsorbent is never completely unfreezeable. The amount of water in these two divisions varies as the absolute amount of water goes up, but it appears that even if there is a relatively small amount of total water present, some of it is still seen as a freezeable component. Thus one still sees a very small heat of fusion peak.

Unfreezeable water appears to behave as a classic amorphous diluent. It seems in this system to plasticize the soft segment of the polyurethane that we have studied, and no new concepts need to be invoked to understand what is going on on a molecular level.

CONCLUSIONS:

1. THERE IS A DISTRIBUTION OF ADDED WATER INTO "FREEZABLE" AND "UNFREEZABLE" PORTIONS.
2. "UNFREEZABLE" WATER IS AMORPHOUS: IT PLASTICIZES SOFT SEGMENTS.
3. LOWERING OF T_m FOR FREEZABLE WATER MAY BE A SIZE DISTRIBUTION EFFECT.
4. THERE IS EVIDENCE FOR A DISTRIBUTION OF SITES: A FEW PERCENT WATER MAY INTERACT WITH HARD SEGMENT.

FIGURE 7

I should in addition discuss the behavior around 0°C, the melting point of bulk water. It is a very common finding in these systems that T_m is depressed. It is possible that this is not a consequence of the interaction of the matrix with the water, as this phenomenon is usually attributed to. Thus we have examined the heat capacity of polyethylene powder, a very hydrophobic system, with small amounts of water. We found a broadening of the melting peak and a lowering of the maximum melting temperature below 0°C, but the area under the peak was equivalent to the amount of water that was added. This implies that there is no bound water on polyethylene, not unreasonable, but even without such binding the phenomena which I mentioned occur.

It seems to me what is probably happening is simply due to a capillary effect, and, one does not have to invoke interactions of surfaces with water to see this sort of thing. This is possibly an oversimplification, but I think it is a good working hypothesis.

Finally, with respect to the systems I have discussed here, we find that there is a site distribution, in other words, some of the water goes to the hard segments which have a small but not negligible amount of hydrophilic kinds of groups.

These kinds of measurements, it seems, offer an extremely valuable insight into the interaction of water, or any small molecule with a solid macromolecule. They should surely be of considerable help in the epoxy problem considered here.

DR. MCCULLOUGH: We will move on now to the topic, Non-Destructive Evaluation, and Dr. Kibler from General Dynamics will be speaking rather than Dr. Yee.

DR. KIBLER: Bill Yee was very sorry he could not be here today. I have the dubious duty of presenting his view graphs. There were thrust upon me upon leaving, and I feel an incredible license to say whatever I want about them. But you will find that the message, I think, will be very simple and the view graphs will be some which you all can readily understand.

For example, the first one. With respect to our product line, we are of course interested primarily in only certain of these examples, namely, graphite epoxy composites, graphite epoxy/metals, and the honeycomb-graphite epoxy skin structures, (Y-1).

All in all, we would like to consider nondestructive evaluation in terms of an overall quality assurance kind of plan, and direct our attention to these four areas: Process Control, Certification involving either NDI or proof-test, Inspection at a manufacturing stage, and finally In-Service Inspection, (Y-2).

We have several problems in non-destructive evaluation. It's rather easy to talk about various kinds of discontinuities that we think may degrade integrity of composites, and we have some examples. It's quite another question to decide what the effects of these discontinuities may be on the performance of a structure, and that overall is the message which I bring to you today: the problem of the effects of defects, (Y-3).

We can detect certain sizes of defects, which I will talk about. We can detect certain types; we can find out

I. INTRODUCTION

I-A Definition and Examples of Composites

Definition: A mixture of two or more homogeneous materials or elements

Examples: Graphite-Epoxy

Boron-Epoxy

Graphite-Epoxy/Metal

Graphite-Epoxy/Honeycomb Core/Graphite-Epoxy

Boron-Epoxy/Honeycomb Core/Boron-Epoxy

Metal/Metal

Fiberglass

Metal Matrix

Y-1

II. QUALITY ASSURANCE PLAN

- A. Process Control
- B. NDI vs. Proof-Test
- C. Inspection at Manufacturing Stage
- D. In-Service Inspection

Y-2

III. OBJECTIVES OF NDE

III-A Defect Definition

Discontinuities that Degrade the Structural Integrity

- Delamination
- Void
- Inclusion
- Fibers separated from the matrix
- Cracks in matrix
- Broken fibers
- Resin-rich fibers
- Resin-poor areas
- Undercured
- Overcured
- Etc.

III-B Defect Detection

- Defect size
- Defect type
- Defect location

III-C Process Control Monitoring

- Inspection of raw material
- Handling procedures
- Ply counting
- Fiber orientation monitoring
- Monitoring of curing time, temperature, and pressure

III-D Property Measurement

- Velocity of sound
- Density
- Thermal conductivity
- Electrical conductivity
- Resin content
- Tensile strength

III-E Defect Characterization for Fracture Mechanical Modeling

- Defect type characterization
- Defect growth monitoring
- Probability of detection of a defect type

where they are. But the question of whether these defects are harmful in terms of degrading structural performance is quite another question viewed in a broader sense. Let's look at process control monitoring. We do very little of this, frankly, in terms of non-destructive evaluation. It's something that I know many people are doing and we think should be done. One can look to non-destructive evaluation for measuring properties, even mechanical properties, which one might otherwise do by other methods.

I will talk briefly about the last topic, namely, given a defect (whatever that means), can one follow the growth of that defect under certain kinds of environmental histories and say what will happen to the structure?

Let's see. This is a "golden oldie" view graph (Y-4) as you see the date from September, '70, but it's still applicable to some extent. We have a 50-ply graphite epoxy composite. I think that should be more like a quarter of an inch instead of a half-inch as the figure indicates. We have put three thicknesses of fiberglass inserts into the composite when it was laid up, and we have taken X-rays of it. Well, as you might expect, one can detect all the defects, even the thinnest ones. This is a radiographic negative that was enhanced by an image quantizer. The problem is what does a fiberglass insert have to do with the real world? We will readily admit to that question. One can even get more sophisticated. The (Y-5) next figure is a titanium wedge structure with graphite skins. Once again, fiberglass inserts at semi-random locations, all

Image Quantizer Recording

OF X-RAY NEGATIVE OF 50-PLY GRAPHITE-EPOXY

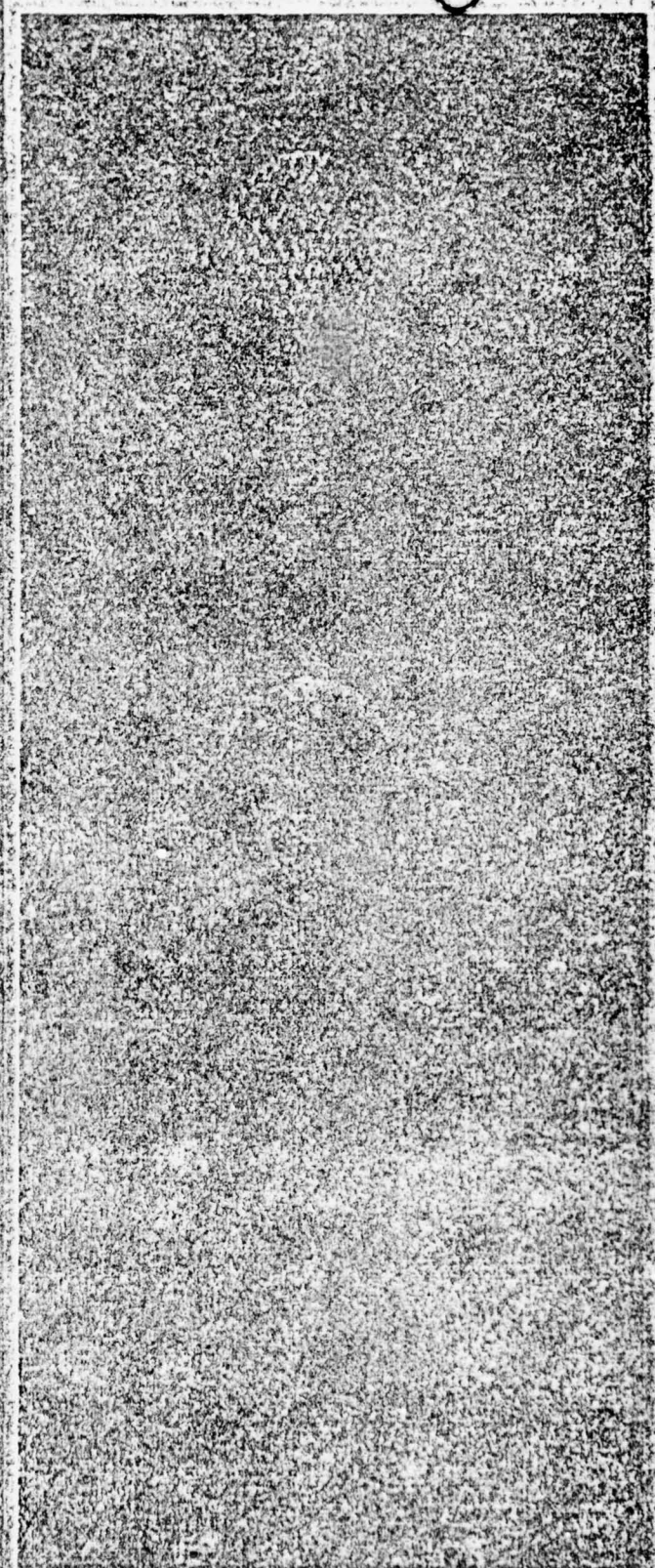


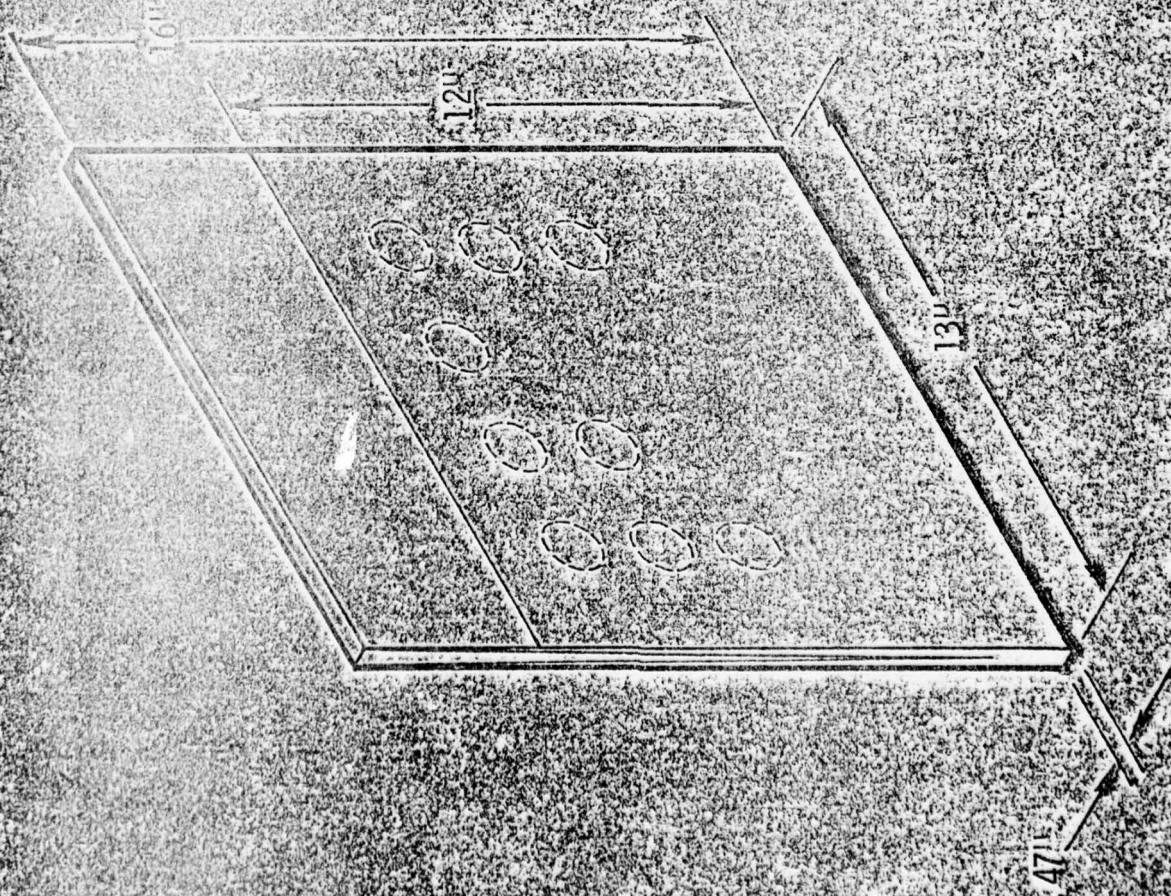
Image Quantizer Recording of X-Ray Negative of a 50-Ply (1/2-inch Thick X 4-inch Wide X 12-inch Long) Graphite-Epoxy Lamina with Three 1/4-inch Diameter Fiberglass Inserts of 1, 3, and 9 Mills Thick. X-Ray taken at 25 KV

100-257-106-224

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FW 74-22-UG4717
4 APR 1974

Titanium Wedge with Graphite Bonded
on Both Faces to Form a Specimen
of 1 1/2" x 13" x 16". Nine 1/2" Dia.
meter Fiberglass Inserts of 4-1/2 Mil
Thick were Placed Between One
Interface of Graphite-Titanium



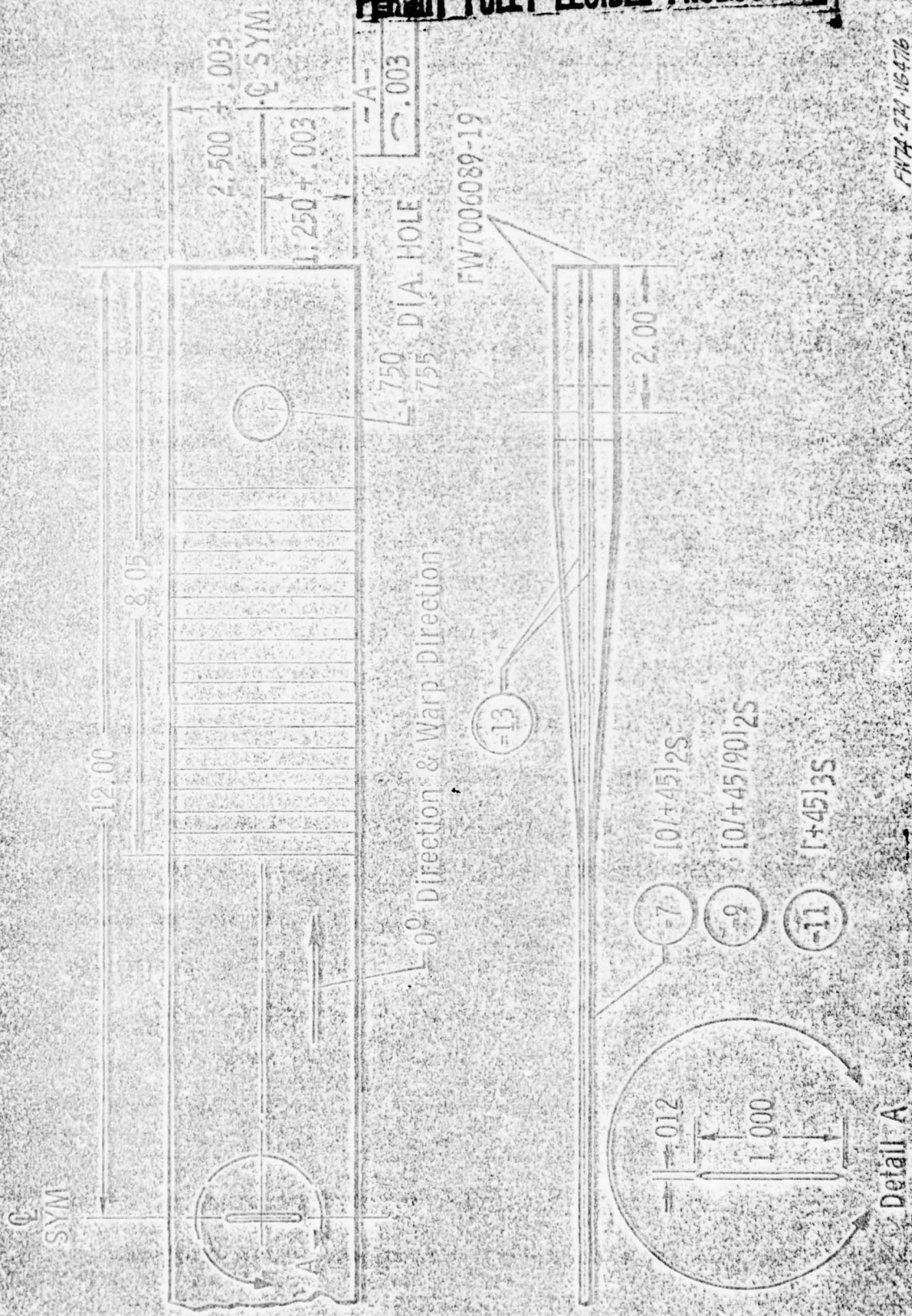
of the same size and all of the same thickness. If we do an ultrasonic C-scan of this, we can in fact find some of the defects and some that we didn't know were there. (This, of course, is not representative of our usual manufacturing.)

Moving right along to growth of defects and discontinuities, very much related to crack propagation, as Wolfgang mentioned, the next figure shows a typical fracture toughness specimen, a graphite epoxy coupon with some kind of notch (Y-6) in it from which we expect some type of damage to propagate when this coupon is subjected to some kind of environment. The environment specifically in this case was simple ramp loading, and we have done a fairly straightforward thing. What we see is the sequence of X-rays taken at the end of the notch, which you saw on this specimen. The numbers refer to the particular stress level at which the X-rays were taken, and in each case we have doped this region of the composite with an opaque additive, tetrabromoethane, in this case. We are also evaluating Renografin for this purpose. As the stress level is increased in the specimen, this is a ± 45 degree specimen, one in fact sees some type of damage beginning to emanate in 45 degree directions from the edge of the notch. This specimen failed at slightly over 11 ksi, so we have some kind of damage under a load history. The question is, what does it mean?

The next figure is a similar type of sequence of X-ray negatives, in this case on a π by 4 specimen where one sees both ends of the notch, and in this case the damage is not

AS

ERACTURE TOUGHNESS SPECIMEN DWG ACD 73002



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FW74-274-16476
4 APRIL 1974

Flaw Propagation under load in

so nicely localized along fiber direction, but in fact tends to be perhaps a conglomeration of various kinds of damage. We can plot the lengths of such damage for different directions corresponding to fiber directions as a function of load history. This is very straightforward to do, not quite so straightforward, perhaps, to interpret, (Y-7).

In fact, we can get even more sophisticated and instead of simple ramp loadings we have in the next figure subjected the same type specimen to a random flight-by-flight F-16 spectrum, and one can plot the type of damage to the mean lifetimes in this case, (Y-8).

So what have we found? We have found basically that we can detect certain types of defects, but what do those (Y-9) defects mean? We believe that at least from our standpoint the areas of primary importance are these. What is a defect initially? We have to work with the right people to define what defects are critical in terms of degrading structural performance. Once that is done, can we simulate such defects? It's easy to simulate defects which you can detect. That is, if you know that you want to detect something it's somewhat easier to know how to simulate it to make sure you detect it.

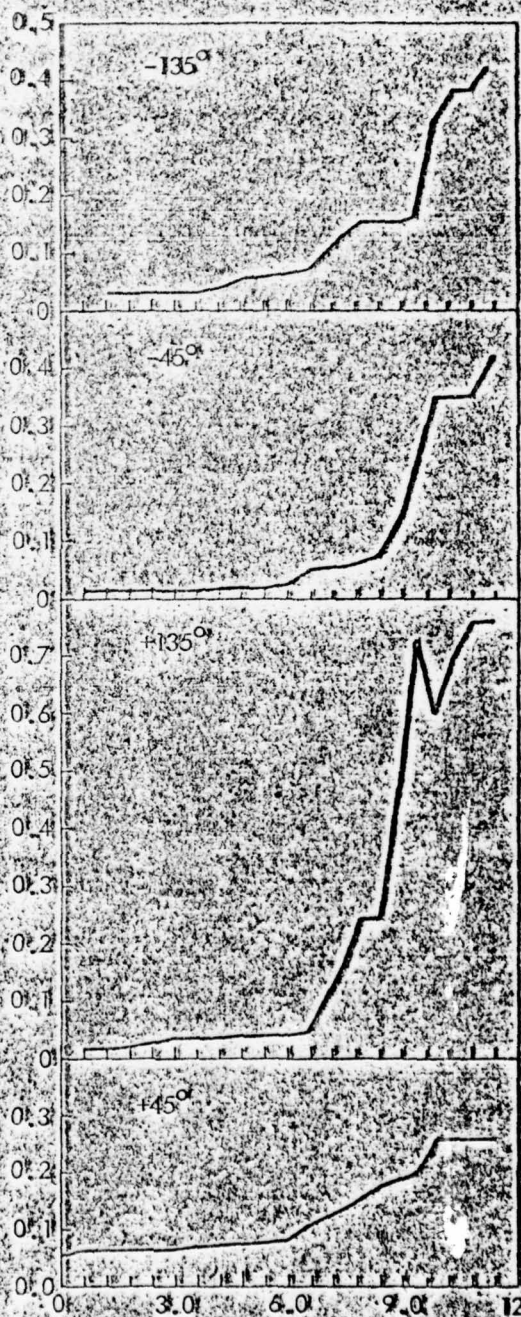
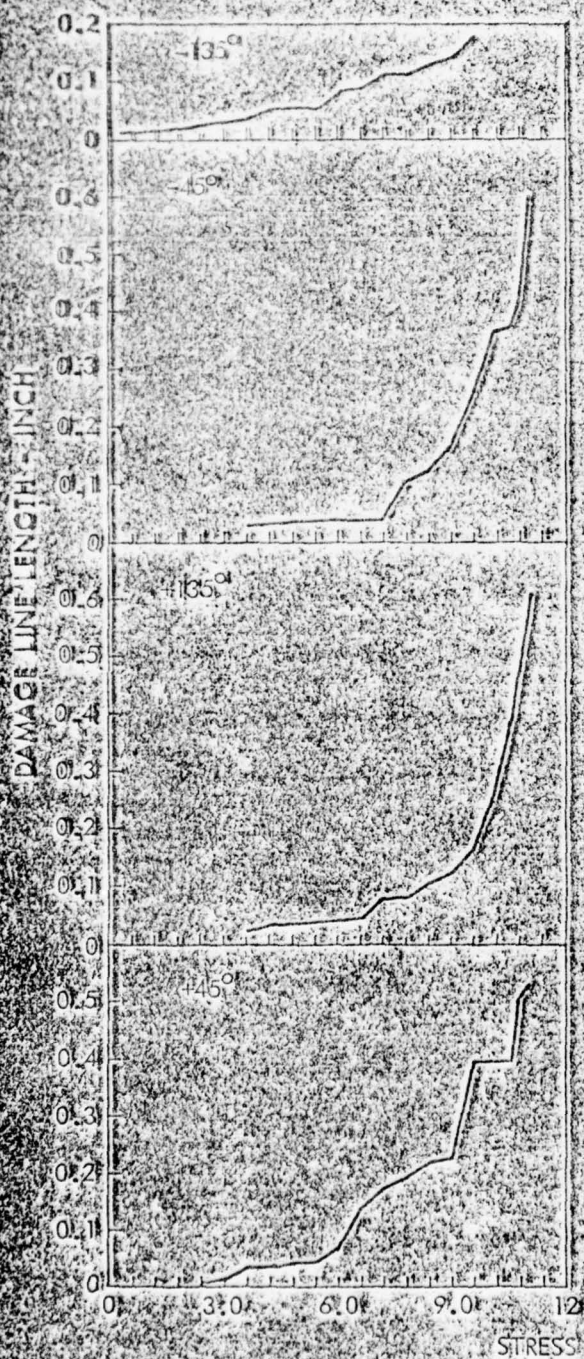
It's quite another question to simulate something which may be realistic. And, finally, if we have decided what defects are and if we know how to simulate them, then we need to do extensive investigations under realistic kinds of environment and load conditions.

The other two areas, which we would like to work in

DAMAGE LINE GROWTH FOR $[\pm 45]_3 S$ SPECIMENS UNDER RAMP LOADING

SPECIMEN 3-5

SPECIMEN 3-2



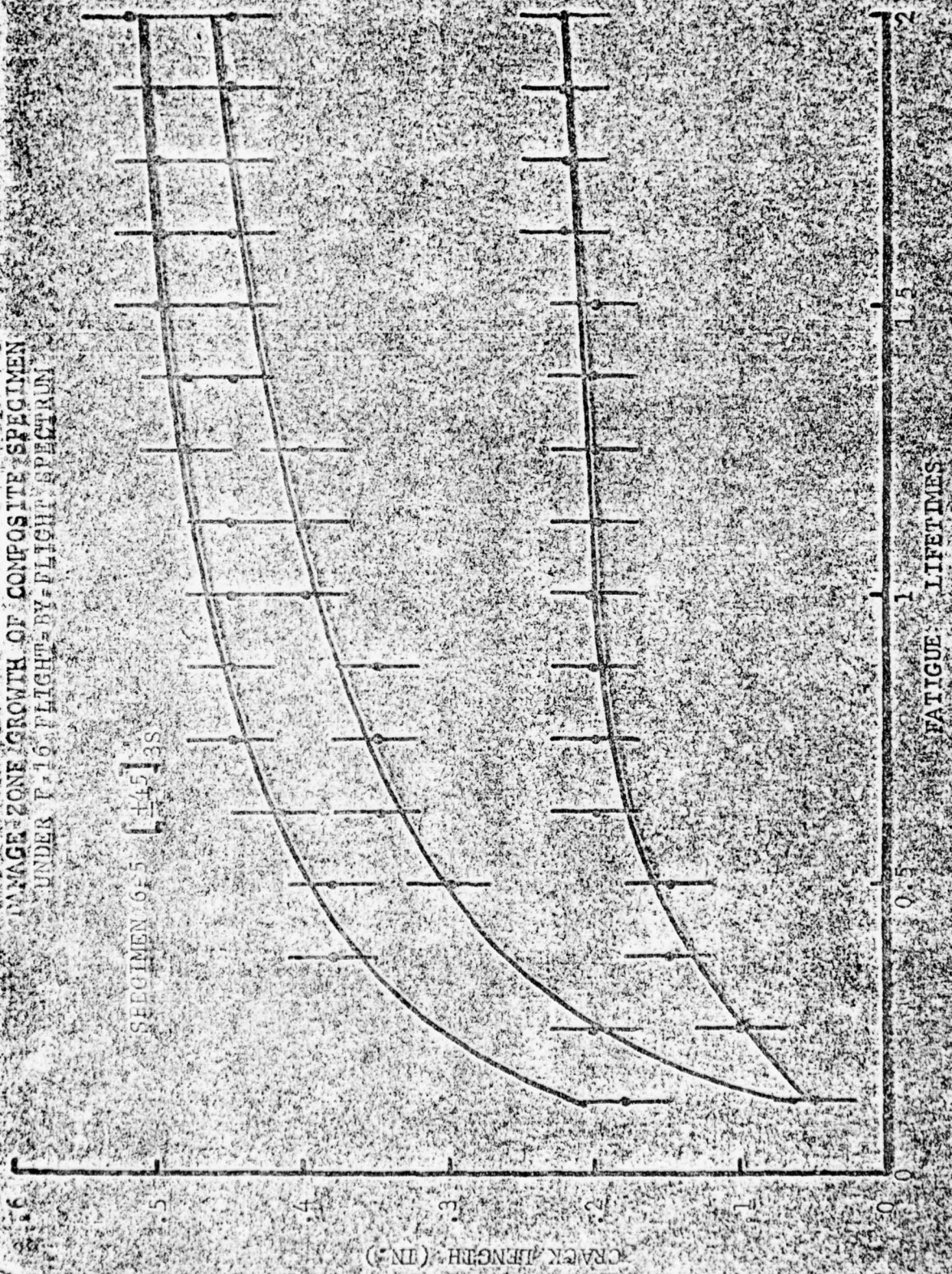
STRESS LEVEL - KSI

FIG. 11-16-47
4 APR 1974

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DAMAGE ZONE GROWTH OF COMPOSITE SPECIMEN
UNDER F-16 FLIGHT-BY-FLIGHT SPECTRUM

SPECIMEN 6-5 [145] 3S



RECOMMENDED FUTURE WORK

1. EFFECTS OF DEFECTS
 - o WORK WITH STRESS ANALYSTS TO DEFINE CRITICAL DEFECTS
 - o LEARN HOW TO SIMULATE SUCH DEFECTS
 - o CONDUCT EFFECTS-OF-DEFECTS INVESTIGATIONS UNDER REALISTIC CONDITIONS (ENVIRONMENT AND LOAD)
2. CONTROL OF INCOMING MATERIALS AND PROCESSES
3. IN SITU MEASUREMENT OF MOISTURE CONTENT

more extensively, are two that I only touched upon briefly: use of NDE for controlling incoming materials and processes during manufacturing, and finally this last one, which I don't believe hardly anyone has addressed to any extent today (I would like to talk to anybody who is doing any work in this), namely, how does one measure in situ moisture content and distribution on aircraft in the field, for example?

Thank you very much.

DR. MC CULLOUGH: Our final speaker is Dr. Levy from McDonnell-Douglas.

DR. LEVY: At this late hour of the afternoon, I am glad to see that many alert faces surrounding me.

Well, the short-term effects of absorbed moisture and high temperature properties of resin matrix have been identified mainly as reversible phenomena. The plasticization of the resin matrix by absorbed moisture, which on the molecular level means disruption of inter-chain hydrogen bonding, has also been identified as the principal mechanism of the moisture effect.

Now, considering the elements of the anticipated surface environment, that is to say the stress, elevated temperature and moisture, and what is known on the behavior of other polymers under similar conditions, the possibility of small but cumulative irreversible change in the resin matrix likely to affect the long-term durability cannot be ignored. And the program designed to investigate this aspect of the moisture

problem was formulated by the members of the polymer branch at AFML, and notably, Dr. Ivan Goldfarb, and is being pursued at MDRL with contributions by a number of scientists, two of whom are here, Dr. Wolfe and Dr. Morgan.

The selection of a suitable resin system for these studies was the first order of business in that program and there was a need to carry out the experiments with a chemically well-defined resin system, but also there was a need to obtain data on the relevant resin.

So we selected for these studies the NY-720 cured with DDS, which together, essentially represented two main complements of the 5208.

Now, the selection of a research tool capable of detecting minor chemical changes in a three-dimensional epoxy network was also a main item on the agenda early in the formulation of a research plan, and since this session is devoted to non-destructive testing, I mean these two lectures at least, I will devote some time in general terms to discussing the advantages of the tools that we have selected.

Before that, I'd like to look at what are the potential chemical changes likely to take place in the resin matrix as a result of exposure to the stress, temperature and moisture environment. I would like to see the first slide.

The objective was to seek evidence for occurrence of irreversible chemical changes. As I said in specimens exposed to stress, elevated temperature and moisture, which we called abbreviated STM, and I'd like to use that abbreviation for

later on. And the potential processes that, or chemical changes that could take place are listed here. We could have crosslinking reactions leading to embrittlement, which can continue due to enhanced molecular mobility in the plasticized resin. And this phenomenon has been, I guess, observed recently by Dr. Browning of AFML, and he will probably be reporting on that finding, and I imagine other people might have seen similar effects. [Eds. note: Artwork is not available].

Now, the next item here is a similar thing that is the stress-induced bond cleavage, which occurs in many polymeric systems of course in the creation of free radicals which are capable of further reactions. I'd like to sort of skip that because everybody is well aware of that.

Now, the third item is the one that I would like to discuss a little bit more in detail, and that is the stress activation of chemical bonds leading to increased probability of hydrolytic or any chemical reactions in the polymeric system. That could be defined more like what could be called mechanochemistry in polymers, and that is an aspect which has kind of been ignored.

What happens is when stress is applied to levels before a bond occurs, there is stress in different distances and changes in angles of valence which leads to potential change of energy of the system and then reactions with molecules surrounding that, particularly activated molecules such as water, they could react, that will lower the activation energy for the reaction, and without the stress what might not have occurred could,

under these conditions, occur, particularly if we add to that the consideration of high temperature.

So this is kind of a justification or sort of a reasoning behind that fear that something like that could happen in the polymer system.

Now, one of the difficulties, I'd like to discuss it in the next slide, some of the difficulties that I encountered in the detection of minor chemical changes in cured epoxy matrices, I am sure that anyone that has ever been confronted with that aspect is fully aware of it. Being totally insoluble and infusible there is only a limited number of things that one can do with the cured epoxy system, and we don't want to work with model compounds, because findings on model compounds do not always translate into the real systems of a complete polymer.

Now, the infrared spectroscopy, which is usually the first thing that comes to mind to anybody that's talking about changes, chemical changes, in the cured epoxy, is not equally sensitive to changes in physical chemical moieties, and one particular change in hydrolytic demolition, and that is the presence of orange groups; they are abundant in the resin anyway to start with. So we don't have the hydrolytically degraded OH's crying loud to us, "Here we are," or something like that, waving a flag, or something of this kind.

So these are some of the difficulties that I'd like to mention here.

When trying to find then the research tool that will be

suitable, we looked into all instrumental techniques, into the kind of information that they can produce on the cured epoxy system: Is it NMR, ASR, mass spectrometry or any other techniques that we can think of, and we concluded that a recent development in infrared spectroscopy, and that is the introduction of Fourier transform spectroscopy, is the one area which offers a chance of detecting the minor chemical changes that we are talking about, and I'd like to discuss the principle on which the Fourier transform spectroscopy operates, with the intention of perhaps awakening an interest in you in that particular new development. And whenever other members of this forum have a need to determine minor chemical changes for aging studies or anything, they should always consider that particular tool, which has been used for the last several years, and is gaining popularity, and essentially is revolutionizes infrared spectroscopy.

The Fourier transform spectroscopy is based on the Michaelson interferometer, which is schematically shown in this slide. It consists of two perpendicular mirrors. One is fixed and the other one is moveable. And a big splitter - the source of radiation that comes in is being split into two parts. Half goes into the moveable mirror and part is reflected through the fixed mirror, going through the detector, through the beam splitter, back again, and these two beams recombine again, and when the mirror, moveable mirror, moves they would constructively or destructively create an interferogram at the detector. If we put the sample at the exit

of the beam between the detector, maybe at this point here, between the interferometer and the detector, the certain frequencies of the interferogram will be absorbed by the material. And we are going to get an interferogram which is characteristic of the sample and the constant characteristics of the interferometer, and when one gets an inverse Fourier transform of the interferogram as shown on the next slide, typical interferogram, in which there is a displacement of the mirror, and you have the intensity of the light - this is not a monochromatic light, but it's a white light which combines all frequencies together of inverse interferogram of that, one obtains the regular spectrum.

Now, the question may come as why, if we end up with the regular infrared spectrum, why do we have to go all through that exercise of a computer transform and so on? The answer to that question, of course, would be the fact that Fourier transform infrared spectroscopy offers a number of advantages which are listed on the next slide. The so-called Fellgett advantages that the information from all frequencies of the spectrum is gathered simultaneously, leading to a tremendously improved signal-to-noise ratio, as a matter of fact, between 100 and 200 times in improvement. So we have a great improvement of sensitivity there, and one can obtain infrared spectra from much smaller quantities of material. And in our case that not necessarily is important, but in some cases, for people that study monomolecular layers, some cases of people that are possibly interested to look into the fibers coated or treated

with certain chemicals that might be a way to do it because of the tremendous sensitivity that is offered. And Jaquinot's advantage is because there are no splits in the system, there is an improvement in the optical throughput of about 40 times as compared for dispersive systems for a comparable optical resolution. And the Conne's advantage, which again gives a large advantage to the frequency accuracy, which was one of the most surprising things to me, because looking at the interferometer I could not see how that could give a more accurate frequency measurement than a dispersive system.

These are, of course, the interferometer type of based advantages. The biggest advantage of course is that all that data is available in a digital form to be able to perform for the manipulator or the operator to do a lot of arithmetical manipulations of subtraction, multiplication, by factor and so on, which greatly enhances the ability to detect minor chemical changes, because one can subtract the differences, subtract the infrared spectrum of a specimen before and after exposure and thus seeing the net changes that have taken place.

Now, if all that was needed for us to get that, to get the right results, was just to get the integrated Fourier transform infrared spectrometry, that would have been a pretty nice thing if you just buy an instrument, put the sample in, and get the results out and type in subtraction routines and so on.

Unfortunately, things are never that easy, and the requirements of the experiments, that is, to expose the samples to stress, elevated temperature and moisture, were such that

we could not work with thin enough samples that will be adequate for transmission infrared spectroscopy.

So we had to resort, we were more or less forced to resort to the more complicated and more difficult internal reflection infrared spectroscopy, which is the difference between the two shown in the next two slides. Here is transmission and here is reflection. When there is a crystal and the sample is attached to it in intimate contact with it and a beam of light is reflected there is also penetration within the sample, and one can obtain infrared spectra of the reflected spectrum, which is similar to the transmission spectrum, not identical the way it's shown here, and the differences vary from one spectral region to another, and one always must think in these terms too.

The next slide shows a little bit more detail on that particular aspect of internal reflection spectroscopy. There is a certain depth of penetration, which is a function of the wave length, and in our case we are talking on an average of a penetration of 10 microns, which is not much, so, essentially, we are looking close to the surface and we are at all times kind of saturated by the moisture in the system.

So we didn't have as much to worry about moisture gradients except from the point of view of distribution of the stress that we were applying.

Now, the next slide, very good, is very well synchronized, it shows - here we are switching from one mode of operation to another. I wish in my lab everything went as smooth. This

shows the internal reflection attachment, which was the first commercial internal reflection attachment for Fourier transform spectroscopy that was made, and this is a laser beam here. Just to visualize what happens is that the beam you see reflected and concentrated, the specimen is clamped here to the crystal, there is a crystal that the beam goes through it, I don't know how visible that is, but each time there are multiple reflections the beam comes out of it and continues its path on the other side, going this way, and essentially the beam, if there was no attachment here, would have gone straight to the detector, and this kind of interrupts that path and puts the internal reflection attachment to it, in this optical path.

The next one's a little bit more close and you can see perhaps a little bit better that epoxy specimen here the way - before and after - which is clamped in that position before and after stress is applied, and the beam impinges on this end of the crystal and goes through the other. Unfortunately, the use of internal reflection spectroscopy and in conjunction with Fourier transform spectrometry is not enough off-the-shelf capability which one could buy the equipment and start getting results, and there is a lot of trials and tribulations that go into the process, and there are a number of difficulties in obtaining a reliable internal reflection spectra which is sufficiently reproduceable to be able to give you confidence in the minor chemical changes that you are looking at. And that requires a lot of experimen-

tation, and in trying to figure out where are the sources of error in the experimental mounting procedures, the pressure that you apply, any possible coarse contamination of the surface and a number of phenomena of that nature.

So there is a warning to be sounded in anybody who is thinking in terms of Fourier transform reflection spectroscopy. But it's still a very powerful tool.

With that, I'd like to proceed to a description of an experimental scheme that we did in order to conduct the experiments we were doing.

Next slide here.

First, we start with the casting and curing of the specimens, usually 15 to 18, and we divide them into two groups, and all the ones - we measure the Fourier transform internal reflection i.v. spectra before treatment. Then some of the path of the specimens will be exposed to STM environment and pass into control environment, which is just stress and temperature. Then the ones that were at STM will be dried and the post-treatment exposure will be anywhere between four to ninety hours or eighty hours, to be exact, and then we have post-treatment Fourier transform i.v. spectra, and we get two types of i.v. spectra, the STM minus ST, and the other one is the post-cure, that is between two different samples. I mean they were cured together and they were cast from the same mixture of the resin, but nevertheless they were in slightly different environments, so we have these two differences. The post-cure minus the pretreatment, which this

one gives the net chemical change as a result of the particular environment in each one of these environments, and this one gives the, sort of the net effect, which is strictly moisture-related and not, you know, as compared to the - this gives the strictly net treatment type of effect.

Now, the next slide shows an infrared spectrum of an MY-720 plus DDS uncured and which shows some of the bands which we detected differences in, some of the differences are the ones I'm talking about. These three bands that we see here originate in the sulfone bands of the DDS, and they represent the symmetry and asymmetry stretching vibrations of the sulfone band in the DDS.

There are two other bands here that also show in the sulfone band. However, unfortunately, in this region of the spectrum the Fourier transform system and the internal reflection mode is not as reliable. The error is multiplied here. It's increased. And we could less rely on the data that we were getting from this region.

Now, the 1500 absorption band comes from the benzene ring, and there are benzene rings in different environments here, so it's a composite essentially, that absorption band, which looks pretty sharp here, later on after curing broadens and consists of a number of benzene rings in a number of different environments, and therefore that kind of complicates slightly the interpretation of what happens in that particular region of the spectrum.

What we see is the degrees of these two bands, and they

are shown in the next slide, plotted against - this particular one was an 1142 band, and it's plotted here in the following way, the Hi-ST and STM, Hi means high stress, Hi because we were varying the stress level from 30 kilograms per square centimeter, which was at the edge of the elastic limit and going above it up to the 90 kilograms per square centimeter, which is well beyond the elastic limit. So we knew that we were breaking bonds, but nevertheless we wanted to see the effect and the kind of things that happen under these conditions.

So as we see here, the levels are within the area of these two and within the area of these two, and then we have the other sample which is again pretty close, the untreated sample, which is then the area, but as we go to the sample exposed to temperature-moisture without stretch, and we have the lowering and again lowering of the low STM and Hi-STM, so there is a decrease in several per cent of the DDS band. And the next band is even more dramatic as you can see it here, it is up to 7, 8 per cent decrease in the sensitivity of that particular band.

Now that sounds like too much to expect, and the question is what is the mechanism that is causing that? And we have a speculative type of suggestion of a mechanism which is shown in the next slide. And from thermal degradation studies they have found - thermal degradation studies of polysulfone, they have determined that when the carbon sulfur bond is the weakest in the chain, and that is the first one to

rupture, and once a radical is formed here, due to rupture of this bond, spontaneously, SO_2 is evolved, leaving the chain with two radicals that, you know, later on react to grab a hydrogen from somewhere.

Now, we have no rigid proof for that, but it's something that has been seen, and it explains the type of data that we are getting. And further data has been coming pretty rapidly, and we might be able to either prove or disprove that particular hypothesis in the future.

But the next slide gives sort of a summary of conclusions, and as you will note, I have put a date on that, because these stages we have a lot of data that's been looked at from different points of view, and maybe in a week we might have a slightly different set of conclusions, but nevertheless so far we can say that no evidence for purely hydrolytic reactions was found. But we have to also say that such evidence will be difficult to be determined because of the nature of the experiment and the fact that we have a lot of that group in cured epoxy systems.

Now, you observed the decrease of sulfone bands that we just finished talking about. This could be interpreted as a secondary effect with the water plasticization. What we are saying is the resin is plasticized and due to the increased mobility, we are concentrating stress on certain crosslinks in the system and on certain bonds, and the weakest bond might sort of rupture, whereas an unplasticized system we have a more rigid and perhaps different type of distribution of

stress, which is less likely to lead to bond rupture of this kind. And another conclusion that despite the difficulties and the troubles that I mentioned I am still confident that Fourier transform i.v. emerges as a powerful tool for non-destructive studies of minor chemical changes in resin systems.

Thank you.

DR. MCCULLOUGH: Thank you very much.

MR. WALKER: I would like to take this opportunity to thank the speakers for their time and effort, and the gentlemen here who are so efficient at running these machines better than some laboratories.

(Dinner Recess)

E. Evening Session - Continued Discussion

MR. WALKER: Without further ado, let me open the floor to anybody that would like to comment, question, discuss, make observations, or as you will. George, you are right on.

DR. SENDECKYJ: Recently, I started looking at the Soviet literature dealing with the moisture problem. The Soviet journal Plasticheski Massy (translated as Soviet Plastics) is publishing quite a bit of work on moisture absorption and moisture effects in all sorts of polymers and composites. There is a lot of foreign language literature on the moisture problem that is not recognized in this country.

I have a bone to pick with Dr. Phil Francis, who commented that there have been no attempts to do the micro-mechanics analysis for the diffusion equations. The Soviets have published a number of papers on diffusion in composites.* Moreover, most of the work on heat conduction in composites applies to the diffusion problem since the governing field equations are the same.

DR. FRANCIS: That's a bone I am willing to concede.

DR. SENDECKYJ: Okay.

MR. WALKER: Thank you very much.

DR. KARASZ: One of the points that hasn't been mentioned, in fact the word has hardly been mentioned today, is crystallinity. If you asked me what to do about what you call "degradation," what I call lowering of the T_g , I would say put some crystallinity into it.

* See, for example,

G.A. Van Fo Fy, "Diffusion in Reinforced Bodies" (in Ukrainian), Dopovidi Akad. Nauk UkrSSR, Series A, Fiz.-Tekhn.-Mat. Nauk, No. 10, 1967, pp. 891-894.

V.V. Bolotin and V.N. Moskalenko, "Macroscopic Coefficients of Heat Conduction and Diffusion in Micro-inhomogeneous Solids" (in Russian), Prikl. Mekh. i Teor. Fiz., No. 6, 1967, pp. 7-13.

G.A. Van Fo Fy, "Basic Theory of Diffusion Processes in Reinforced Media" (in Russian), Prikladnaya Mekhanika, Vol. 4, No. 9, 1968, pp. 23-32.

Let me just show you what I mean, if I may. Everyone's talking about G' as a function of temperature. You have this curve, $\log G'$ and you put in plasticizer, . . . actually this is quite unnoticeable on the log scale, but it's a factor of three or five or ten on the non-log scale. Now, as everyone here knows the way to avoid this is simply to build in some crystallinity.

Now, crystallinity in thermosets is an unorthodox concept. But why not make very long chains, for example, or why not have a compatible system which has got some crystallinity in it? Then, no matter how you plasticized the diluent is only going to affect the amorphous regions--the crystallites will hold the matrix together. I just throw that out for discussion, not knowing if crystallinity can be put into epoxies, but it seems not impossible.

DR. GURTIN: I wrote down some comments on the discussion of the talk by Dr. Francis.

First of all, there is a theory of coupled mechanics and diffusion, developed by Biot and discussed by Rice and others. But more important, in the equations you wrote on the board for coupled mechanics, diffusion, and temperature, i.e. the equations of Crank, there is coupling in the terms involving the time derivatives, which involves a coupling in the energy, but there is no coupling in the fluxes. As I would

guess, just offhand, the coupling in the fluxes is probably as important as coupling in the energy. In particular, I would guess that the heat flux depends on the concentration gradient and the mass flux depends on the temperature gradient.

You also mentioned that there is very little literature on non-linear diffusion with thermal effects included. However, the equations are exactly the same as multi-species diffusion, and there is a large chemical engineering literature on multi-species diffusion, including non-linearities, etc. Also, non-linear diffusion is well studied in the Russian literature, and, in particular, Barenblatt, in the fifties, developed a theory of non-linear diffusion which was the basis for a great deal of work by Russian and American mathematicians. One of the nice features of the theory is that there is a finite speed of propagation for diffusion if the concentration is zero ahead of the wave. But anyway, there is a very extensive theory of non-linear diffusion in the Russian literature.

MR. WALKER: Any other comments? Excuse me. Any discussion on the point Dr. Karasz has made? That's out of my ball game.

DR. FOUNTAIN: Yes. Assuming you can get crystallinity into the matrix, how do you process it with the unidirectional fiber to make a material capable of fabrication?

DR. KARASZ: Well, I don't know. You melt it. I mean, I would assume that there was some point in the thermal cycle when you allow the material to cool down and you develop whatever I suggested at that point. But it's a vague concept, of course.

DR. PATRICK: I would like to comment on this thing about crystallinity. In that regard, this is a concept which shakes people all up. I had the personal experience with a branch of the service which shall be nameless, in which we submitted concepts having to do with crystallinity, and they told me I was full of -

But I think that your point is very well taken, and, by George, if AFOSR is indeed what I think it's supposed to be, they should look at this very seriously.

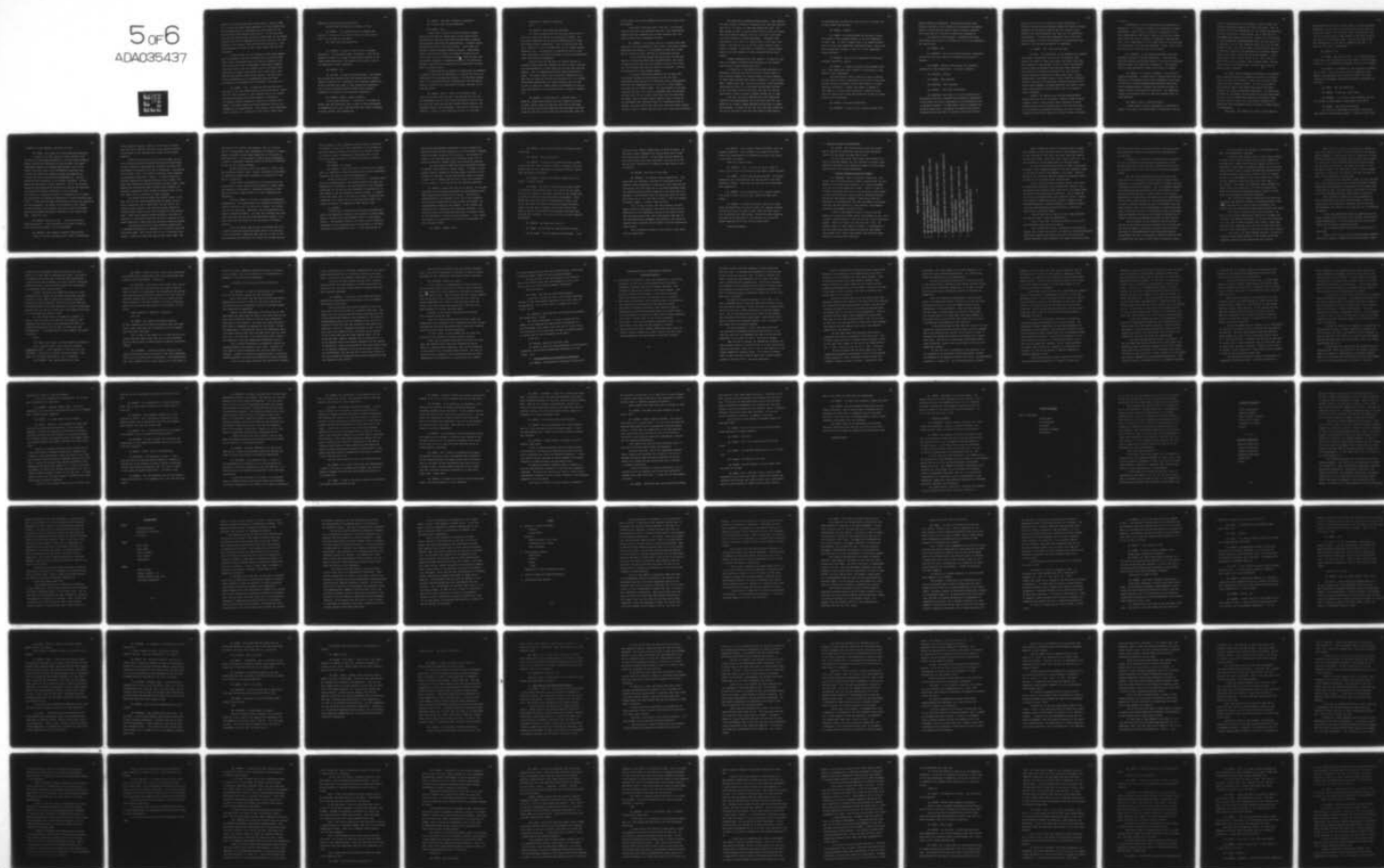
DR. EPSTEIN: I don't think you have to talk about crystallinity, but just some kind of order. We have done a lot of work with non-crystalline materials - not epoxies - but elastomers, and when you look at these ma-

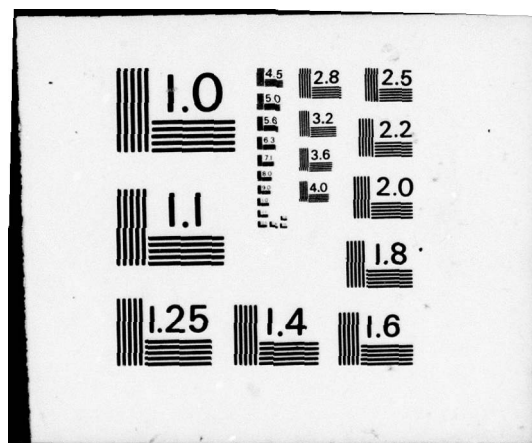
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terials very closely they have a great deal of order to them. It's a point that hasn't been addressed at all by anybody here, but the properties on a microscale are very related to the flow history of the material during cure. I'm not sure that when you are talking about any kind of model that you can simply eliminate the kind of complexity you have in the part, the flow history of the material, and the order that you get on a very localized basis in terms of how it does affect cure and the properties.

In other words, it's not enough to talk about temperature and pressure, but how you design the part and the flow history that the material has as it sets up, because if you take a good close look at elastomers, particularly complex elastomer designs like tire treads, you can find that their properties are highly anisotropic, and I think that is the way this gets back to what you are saying. You don't have to say crystallinity in a conventional sense but order, and order can be designed into the product if you work at it.

DR. KARASZ: Yes. I would just say that the problem here is that the cross-links are being plasticized. That's what the basic problem is. And anything that is not capable of being plasticized, but holds together is beneficial. For example, another possibility would be to consider ionic groups - you make ionomers from these materials that are not susceptible to plasticization. This concept would essentially keep the modulus vs. temperature curve high no matter what

happened to the plasticized crosslinks.

And what you are saying, of course, is true.

MR. WALKER: I'm reminded of Max's comments this morning. If we can do all this in four and a half months, "We've got 'em beat by six weeks."

Any other topic for discussion?

DR. GILLHAM: My name is John Gillham, Princeton University. I'd like some simple information. Does the absorption of water by an epoxy at equilibrium increase or decrease with temperature? The answer will provide a clue to the mechanism of water absorption.

MR. WALKER: Sir?

DR. DE IASI: Mr name is Richard DeIasi, from Grumman. Most people have reported that the maximum moisture content remains a constant as a function of the treatment temperature. We have observed that there is some temperature dependence, and in fact the maximum moisture content does increase slightly as a function of the exposure temperature.

DR. KIBLER: Kibler, General Dynamics.

I will agree with that. I think all of our data indicate that the saturation level is more or less independent of temperature up to say, 240°, and above 240° there is perhaps a slight increase with temperature.

MR. WALKER: Any other comments or questions?

Don, did you want to say something?

DR. ULRICH: Yes.

I would like to point to several chemical aspects. Taking note of what Dr. Morgan said, we are talking about noncrystalline materials that have microstructure, possibly through phase separation and immiscibility. Professor Karasz discussed the role of free water versus bound water and Professor Knauss discussed inorganic glasses. Researchers studying the effect of water in inorganic glasses are concerned about the role of molecular water. Some now feel that the surface chemistry of amorphous materials, the mechanical behavior, and electrical conductivity are determined in large part by molecular water.

In understanding the effects of temperature and humidity on epoxies, which are noncrystalline, we should take into consideration the afore-mentioned factors. The molecular aspects have to be correlated with the supermolecular and macroscopic levels of structure for constitutive property analysis to become meaningful.

MR. WALKER: Well, I think it's precisely right. I think it's correct that Don and I see the need for not only the independent work in the various disciplines involved, but the fact that there has not been enough attention paid to the interface between the disciplines. And that's a critical ingredient, I think, to our technology advance in this area.

There were a couple of questions.

Sir?

DR. BASCOM: Naval Research Laboratory.

I'd like to amplify what Don has been saying with regard to an area that came up in discussion at dinner. We talk about commercial resins such as NARMCO-5208 as if they had sharply define compositions. This is certainly not the case. There is in all of the material we use, fibers, resins, adhesives, etc., a variability of composition that is sometimes intentional, more often accidental, which can dramatically affect the materials properties.

The Air Force and the Navy are funding efforts to establish characterization methods that can be used to monitor the reproduceability of these materials as they come from the vendors. This is something the metals people have had for years. You order a metal, you can get the composition of it. What the Air Force and the Navy are trying to do is to develop established compositions for these materials that are used so that if there is a sudden change in performance we will at least know whether it was associated with a change in composition.

MR. WALKER: I think that is a critical point. I think Dr. Thomas this morning, with his comments of trying to make a point either way from the data that he had seen, until he went back to his laboratory and the people left him alone for two years and he could try and make some sense out

of this thing, one of the messages he said is the quality control aspect.

From some of the data that's come out, I'd certainly hope that as far as the sessions tomorrow in the experimental methods area some comments will be made regarding that, because I think this is certainly critical.

MR. EPSTEIN: I'd like to talk for a minute about something Don, that you alluded to, and I think a few people earlier addressed very slightly. It's something we have had a great deal of experience with, and that is accelerated testing.

I think what most people are doing here is using what amounts to relatively short-term laboratory data, and trying to speculate about how the final system is going to act five, ten, and fifteen years down the road on an aircraft. And you are dealing with a very complex system.

I am going to describe something that we have done with simple systems and the problems you can get into; specifically pipe made out of a basically linear thermoplastic, which has its complexities but in a way is a little simpler than what you are talking about. For years people in the pipe industry have said, "If I want to determine what the behavior of pipe is 20, 30, 40," and in fact they talk "50 years down the road," they do stress rupture testing, which is based on the assumption that long-term creep is a predominant mode of failure, and they develop what they call long-term stress rupture criteria, which is where they plot the log of time versus strength.

But some very interesting things happen. They commonly run these tests for perhaps a thousand hours, and then they project out to 10^5 hours, or some such number like that. But what happens is that if you run these tests a little bit longer than the standards formally call for, you begin to see some very basic changes in failure mechanism. A material like polyethylene, will fail in a ductile mode in this short term regime. But when you run it out for longer times at lower stress it reaches a point where it behaves in a brittle mode, which is just the opposite of what everybody thinks should happen.

Nobody understands why this happens. We know for sure that it's somehow related to the morphology of the systems which we don't fully understand as yet.

On occasion, if the material has been subjected to a weathering cycle you will get this kind of curve, where it will initially behave in a ductile manner and then suddenly at these lower stresses will begin to behave in a very brittle mode. Nobody knows why. And one thing that I think everybody here should be alert to is that when you describe failures in the lab based on short term tests they may not have any application to what is going to happen further out in time.

And, yes, we are not dealing only with crystalline materials like polyethylene, but we see this with PVC, too, which is in a sense a glassy material and has that in common with epoxies. In short you can get into some real trouble if you try to take short term test data without understanding

the phenomenology involved and using the data to project out to much longer time periods.

MR. WALKER: Comment?

DR. KARASZ: The ductile mode for failure is pretty well known in many polymers because of the low temperature at short time. So what I suggest here is it might be possible to do some time-temperature superpositioning. This is ambient temperature testing, I take it, or high temperature testing perhaps?

DR. EPSTEIN: This is room temperature testing and elevated temperature testing.

DR. KARASZ: It might be possible that someone could use a time-temperature shift concept to extrapolate to long rates at room temperature.

The other thing I want to point out just in passing is that there has been a great deal of work done on long term fatigue testing in polymers, and in fact there is a rather important conference, I think, this summer in Sweden on this subject, a fairly large conference. Might be worthwhile for people here to pay some attention to what is talked about at this conference.

MR. WALKER: Any other discussions?

DR. FOUNTAIN: I want to ask a question based on an

organic chemistry background. We have been talking about moisture absorption from a physical and mechanical standpoint. However, rubber modified epoxies used in potting compounds, and coated fabrics "reverted" by hydrolytic degradation.

My question to Roger Morgan. Statements have been made saying that there is no evidence at all for any hydrolysis. Are they correct?

DR. MORGAN: Yes.

DR. FOUNTAIN: You are absolutely positive, completely and utterly sure that there is no hydrolysis occurring in epoxies.

DR. MORGAN: Moisture deteriorates the mechanical properties at high temperatures. Into what, epoxies?

DR. FOUNTAIN: Epoxies.

DR. MORGAN: What epoxies?

DR. FOUNTAIN: 5208, whatever.

DR. MORGAN: I have seen no evidence.

DR. FOUNTAIN: Way back in '71, we did some work on Boron/epoxy 5505 which suggested that hydrolytic degradation of the matrix was partly responsible for the mechanical loss in laminate strength. In other words, when the laminate was dried out there was a percentage of strength which wasn't recovered and we were able to correlate this with infrared

spectra relative to the alcohol and other absorptions. A tentative correlation was obtained between the tensile strength reduction in the matrix direction and the increase in the COM/COC ratio which suggested that there was the possibility of hydrolysis. This has been downplayed, and in fact John Halpin appears to reject the existence of any hydrolysis component in the moisture degradation of composites.

DR. MORGAN: Can I just say one thing?

DR. LEVY: It's refreshing to see somebody that suspects that there is hydrolysis, but you see, bis-phenyl-A type epoxies have been for many, many years surrounded, they have been exposed for long periods of time in marine environments and many other environments and they have shown excellent, particularly the amine-cured bis-phenyl-A's have shown excellent hydrolytic stability for many, many years. We are dealing with a tetraglycol type of resin, which has different chemical moieties in its structure, chemical structure, different bonds somewhat, and these bonds are also known to have fairly good hydrolytic stability when they are in regular organic compounds.

However, the question was are they hydrolytically stable when they are in a polymeric molecule, which is being stressed, and as I said earlier under conditions in which certain bonds could be activated due to the fact that there is an increase of interatomic distances and so on, you are lowering the activation energy for certain chemical reactions

to occur.

Nevertheless, I am not discounting the possibility of hydrolysis. If it occurs, it seems to be occurring, it could be probably a small effect, it would be a question of, you know, maybe sub per cent type of level or one per cent, something like that, and it could be a cumulative, long-term process. But it definitely is not a large effect of the kind that you encountered in the potting compounds. There, I don't know what they were, maybe they were one of these.

DR. FOUNTAIN: In the potting compounds it was predominantly polyester linkages hydrolysing. There has been work done showing that cations present in the matrix accelerate moisture ingress and hydrolytic degradation. The plastics used in these experiments ranged from acrylics to epoxies.

DR. BASCOM: Let me make a comment on this issue of moisture resistance. In recent work in making bonds that must stand up to high peeling forces while submerged in sea water, we find that a simple bisphenoldiglycidylether epoxy cured with a polyamide-adduct (vesamid) but without the usual inorganic fillers has exceptional durability. The commercial highly filled counter parts are much less durable under the same condition.

DR. WOLFE: Wolfe, McDonnell-Douglas.

I think that in terms of hydrolysis or reactions in water, if you want to go high enough in temperature, and any-

time you take anything it's eventually going to react, and then the subsequent products will react with water. Now, if you want to call that hydrolysis, you can always get hydrolysis you know if you heat it high enough. But in the work with the NARMCO 5208, which, by the way, is about 70 to 75 per cent of the tetraglycidal diaminodiphenyl ether, and the rest of it is garbage, a lot of other words for that, but a lot of other things in there, but even with what we have we don't see a lot of reaction on what we call hydrolysis at reasonable temperatures. But, again, if you want to go high enough - a neat resin doesn't have a lot of filler in it. But if you get more filler in it, of course, that's another story. But anytime you want to go high enough, put water in it, you are going to get a reaction.

DR. LEVY: We are addressing ourselves, in a continuation of this program we are addressing ourselves to the problem of contact with graphite, contact with the other interfaces, how they chemically modify. We are not discussing the interface itself, but whether the contact with these surfaces can catalyze hydrolytic degradation. In other words, we might mix the powder and then carry out similar experiments and see if we are seeing some hydrolytic degradation there. In other words, we want to do all possible combinations of conditions and environments which are likely to induce hydrolytic degradation.

Impurities, the presence of acidic or basic type of

impurities which are known in other cases to induce hydrolytic degradation. So we want to try these and on top of that any effects of contact. But the resin itself is basically, even it will be proven later on that hydrolytic reactions do occur, they are not to any major extent. They are not like 10 per cent degradation in a few days or something like that. It would be a low rate of degradation.

MR. WALKER: Sir?

DR. GIBBS: Hugh Gibbs, duPont. Did I understand you to say, Bill, that the epoxy resin that doesn't have all these fillers in is not affected by moisture, the T_g is not lowered?

DR. BASCOM: I'm speaking of the resistance to debonding in water. The fillers often found in adhesives (and paints) are hydroscopic and as such are "sinks" for water sorption and presumably accelerate hydrolytic degradation of the resin.

DR. GIBBS: Just the hydrolytic?

DR. BASCOM: In the sea, under stress.

DR. FOUNTAIN: If you are a good formulator you can put fillers in that produce a hydrophobic epoxy matrix.

MR. WALKER: Any further discussion?

Dr. Jones, you mentioned to me earlier that we not lose sight of the interface problem. I wonder if you'd care

to amplify on your comment, your point of view.

DR. JONES: Bill Jones, Air Force Materials Laboratory.

It occurs to me that there are great benefits to be derived from the polymer mechanicians, and the solids mechanics people conversing; addressing the same problems, from phenomenological behavior to hardware applications, and it also occurs to me that there is an intermediate discipline that is directly involved in adhesive bonding and composite materials, and that is the surface physi/chemistry. We have people here who specialize in the polymer chemistry. We have people who specialize in solid mechanics. But in the physical systems we are dealing with, structural integrity and durability at the physical material interfaces is also required. I think there is a substantial amount of information to be gained by talking with the people who specialize in surface physical/chemistry. I think they can make contributions in areas that pertain to the bond strengths, the nature of the material in the region of the interface, the intrusion rates which might be different from the bulk media intrusion or diffusion rates; things like that. Thank you, Bill.

MR. WALKER: Thank you, Bill. That's an extremely significant point. If we overlooked it, we didn't intend to, and I am sure you brought it to our attention.

DR. KAEUBLE: Dave Kaelble, Rockwell International.

I gave a talk this afternoon and I think I subordinated

a very important subject, which I think we sort of talked about and didn't address, and that is the essential subject of the design of the interface with regard to the overall composite.

Tradition tells us as we go back and recall the history of glass-reinforced composites the moisture degradation of glass-reinforced composites was ultimately solved by the development of coupling in the age of technology. Dow-Corning, Union Carbide, have a full class of chemicals which suppress the hydrophylic character of glass. In carbon graphite reinforced composites my experience dating back to about 1970 shows that commercial surface treatments of these fibers, which enhance the interlaminar shear strength under ordinary air immersion, predispose these systems and degrade about 35 per cent under full equilibration in water immersion.

The reason that the fibers are treated thusly is the very fact that the matrix systems which are epoxy and polyimide in character, are in fact polar, and the fibers, the ordinary carbon graphite, are non-polar unless treated by oxidized means, either nitric acid treatment for the calorics test. These fiber surfaces became hydrophylic and polar in character, so they match very well the polar character of the matrix materials to which they are married by adhesive bonding.

The point about this is that moisture insensitivity is obtained ultimately by a chemical fix of both the fiber and the matrix bases. And I throw this out as a long-range challenge. I think this point has come up many times today, that

the ultimate fix involves the moisture, that is, involves one of two approaches, very fundamental and chemical in nature, either the system is made water-compatible or the system is made waterproof. If the system is made entirely hydrophobic, it means a fundamental chemical change in the matrix chemistry as well as the surface treatment.

We have heard this point this morning, I think, that the functional groups, ether, oxygens, hydroxyls and secondary or tertiary nitrogen groups predispose the system to be sensitive to moisture.

If the fiber is backtracked in the direction of the coning purely carbon, having only pi-bonding or carbon hydrogen bonding at the surface, a compatible chemistry to this type of non-polar fiber surface is in fact something like polyphenyl.

Hercules H-Resin is in fact an acetylene phospherine polyphenylene. Our studies show it's essentially non-polar in surface gravities, but it's brittle as a board. It's worse than the old phenolics. Basically, you have essentially extended conjugation bonding. You have the bi-phenyl type character extending through the three-dimensional network. So I don't know what the answer is, but the answer is chemical, finally.

If we are saying that we want to eliminate the 30 to 35 percent moisture degradation which seems to be intrinsic in all the advanced composites when they are run out in full time moisture equilibrations, we either have to make the mat-

erials systems in total composite system response, forgiving to moisture, so that it's fully compatible to the presence of moisture, variable amounts of moisture, as a matter of fact; or we have to make it waterproof, which means that it will not accept water in terms of a hydrolytic additive material.

Thank you.

MR. WALKER: Dr. Karasz.

DR. KARASZ: I was just saying I agree with Dr. Kaelble that it's impossible to make these materials totally hydrophobic. Therefore, one has to live with hydrophylicity.

Another possibility is to add blocks or sidechains again which are superhydrophylic and thereby prevent once again the degradation of properties, the plasticization of the important crosslinks, by getting the water absorbed in sidechains or in soft blocks to use the segmented urethane analogy. It doesn't matter that water gets in as long as it doesn't plasticize the crosslinks, so I think this is an approach that ought to be looked at as well, if somebody has some ideas on that.

DR. ULRICH:

I would like to mention one additional consideration; that is the presence of sodium on the surface of carbon fibers. There is evidence that the surfaces contain a large sodium content. The potential effect of an alkali such as sodium on performance can be evaluated from the experience of the semiconductor and integrated circuits. In the construction of

metal-oxide-semiconductor structures, silicon surfaces are passivated with 500-1000 angstroms of silicon dioxide insulator glass by thermal oxidation of the silicon. The presence of sodium at the interface and in the insulator gives rise to device instability, reduced yield, and reliability problems.

Dr. Larry Drzal of AFML has found considerable amounts of sodium on the surface of carbon fibers. If these can form complex chemical systems at the epoxy-fiber interface in the presence of hydroxyls, we may have another issue to consider. I agree with Dr. Kaelble that we have to pay close attention to the surface of the fiber and to the interface chemistry.

DR. MORGAN: I agree with what Don is saying. We did some experiments on unfilled polycarbonate and polycarbonate-glass bead composites and boiled them in water. The unfilled polycarbonate did not degrade at all, but in the composite with the glass beads where we have sodium ions present, the polycarbonate unzipped to the monomer. It was evident the sodium ions were catalyzing the hydrolysis reaction. So in that particular case sodium ions could have a profound effect on the degradation of this particular polymer. I can't speak for epoxies, but certainly in the case of polycarbonate it had a profound effect.

DR. ULRICH: Thanks, Roger.

DR. KARASZ: Are you talking about bis-phenol-A polycarbonates?

MR. WALKER: One last question.

DR. BASCOM: If what you are saying is true, we have a whole new ball game, because if there is sodium on the graphite fibers we are right back to the glass situation, and we have been fooling ourselves.

DR. PATRICK: Brazil has isolated quantities of sodium in graphite fibers.

MR. TOWNE: The issue of sodium on the carbon fibers is certainly very pertinent here, but I think you can gauge the level of sodium, its presence, strictly by the temperature to which the fiber has been subjected in processing. Those fibers that are, well, which are essentially carbon, that are in the twelve to fifteen hundred centigrade processing range, are very high in sodium, just by the process used. When you get up to the 2000 degree processed materials they are very low in sodium. But you still have the same composite degradation.

DR. BASCOM: But they still have it?

MR. TOWNE: We are down to a few parts per million.

DR. MC MAHON: I'm Paul McMahon from Celanese. I can

give you actual numbers talked about in terms of sodium. On the type A carbon fibers, we are talking about 2000 to 5000 parts per million sodium. On the higher modulus fibers we are talking about less than detectable, less than 50 to 100 PPM and their composites all undergo the same levels of deterioration.

MR. WALKER: The floor is back here.

MR. WALLACH: Irv Wallach, Naval Research Lab. Last week there was discussion on effect of environment on the graphite epoxy composites at a meeting we had at NRL and several people said that there was no increased diffusion along the graphite epoxy interface compared to the epoxy itself as opposed to glass epoxies where the diffusion along the interface there was 40, 50, 100 times as great. This was repeated by several people. I haven't seen the data.

Now, if that is true, then this question of hydrophylic nature of the surface, this would not agree with the discussions of the hydrophylic nature of the carbon surface that are being stated now, and at the meeting last week no one contradicted the statement that diffusion rate along the graphite epoxy interface was no greater than that through the epoxy itself.

Now if someone has data to the contrary, that would be very interesting.

MR. WALKER: Let me defer further discussion until the workshops tomorrow. That, perhaps, is a proper thing that needs to be investigated and delineated one way or the other, on the effect of sodium.

There is a question here.

MR. BORSTELL: Yes, I'd like to ask Mr. Towne to explain how he gets rid of sodium as the fiber is heat treated?

MR. TOWNE: I don't know the exact method. The sodium compound's just volatilized by the time you get to the 2000 temperature degree. There are very few that are stable above that temperature.

MR. WALKER: In the interests of Dr. Jones's sanity, I am going to call a halt to this, return the mike to Dr. Vinson.

DR. VINSON: In spite of the fact that all my cross-links are plasticized I'd like to point out tomorrow morning the bus will leave at eight o'clock, come over here, and we will be divided into five groups. Most of you have signed up. For those of you who haven't, you can pick out one of the groups tomorrow and we will tell you which room.

[Meeting recessed.]

F. Committee Reports and Discussion

DR. VINSON: This morning each of the five groups met to discuss the particular areas that were designated, and we will not begin the reporting of each.

For the first group, which dealt with Physical Property Correlation Models, Dr. Ivan Goldfarb of the Air Force Materials Laboratory will present the report for that group, and then chair the ensuing discussion.

1. Physical Property Correlation Models

DR. GOLDFARB: When I originally talked with John Kardos about switching groups I didn't recognize what the consequence of my going first would be, so I think he managed to do me in here by having me go first. First I'd like to indicate that people that were in our group were John Gillham at Princeton University, Roger Morgan at McDonnell-Douglas, Ken Kibler from General Dynamics, Frank Karasz from the University of Massachusetts, Don Ball from AFOSR, Jim Gauchel from NRL, Jim Mar from M.I.T., Hans Borstell from Grumman, Don Ulrich from AFOSR, and yours truly.

I took it upon myself to make a little straw man agenda so we could get things going, and needless to say, (G-1), we didn't really follow it. But we will put it up on the board anyway. That's all right, it's the only one I have. We couldn't make up a whole bunch of slides. I was tempted to use the slides that were running around here that nobody had claimed, but I didn't know whether they would be appropriate for the particular occasion.

PHYSICAL PROPERTY CORRELATION MODELS

1. WHAT IS THE RELATION OF T_g TO WATER UPTAKE FOR STRUCTURAL RESINS?
2. ARE THERE ANY IRREVERSIBLE DEGRADATION STEPS?
3. ARE THERE CURRENTLY GOOD DIFFUSION MODELS WHICH ACCURATELY PREDICT WATER ABSORPTION ~~IN~~ COMPOSITES?
4. HOW DOES SUPERPOSITION OF STRESS AFFECT THE ABOVE STRUCTURE-PROPERTY CORRELATIONS?
5. DOES MOLECULAR ORIENTATION (AROUND FIBERS OR AT SKIN) AFFECT PROPERTIES SUCH AS DIFFUSION?
6. ASSUMING ABOVE, CAN WE DEVELOP A MODEL WHICH WILL PREDICT MATRIX-SENSITIVE COMPOSITE PROPERTIES?
7. HOW IMPORTANT IS RESIN CHEMICAL CONTROL OR "FINGER PRINTING" ON ACCUMULATIONS OF PROPERTY DATA?
8. CAN/SOULD WE FORMULATE A PROCESSING DATA BASE TO INSURE A SAMPLE IS "GOOD" BEFORE WE DETERMINE WATER EFFECTS?

G-1

When I showed this group of questions that I thought were relevant to the particular part of the discussion that we were assigned to, the group, the first thing that came up is they said, "Well, this looks like a pretty good list. We can't discuss it in any three years, no less two hours."

But the first thing that came up is what I had listed as items 7 and 8 probably appeared as the most important items in the minds of most of the members of the group. That is, before we can talk about physical property correlation models, we have got to know what we are starting with.

And so an item of resin chemical control and control of processing turned out to be two important factors. And the question was raised at that time that we are talking about two separate characterization activities. One of these has to do with the fingerprinting type chemical control, leading to a chemical composition quality control, perhaps as was mentioned yesterday, leading eventually to chemical composition type specifications and qualifications, and that is essentially on existing resins.

However, there may be those that have been qualified, for which we have a bank of property data.

That is one item. We see that going on at its rate and anticipate that that will continue.

But, in addition to that, we brought up the need for another set of data, if you will, and that is a well-characterized model resin system, which may or may not be any one of the systems presently being considered for usage, but one for which

we can get the kind of structural property correlations that this particular committee was assigned the responsibility to look into.

So there was a need that surfaced within our group to be able to chemically and physically characterize a well-defined clean resin system for which information of the like of the other items on this list could be gathered and ascertained.

Now, the next item that came up was the fact that there really is a paucity of good structural property relationships, or correlations in these kinds of systems, and this is probably true for two reasons. One, the academic community has probably not been excited by this area because it is one that has evolved through its usage, and it's been variously described as a messy system, one that's not well characterized, and of course, which brought up the previous question; and as a result, we haven't gotten the type of information that you might expect to see of the relationships of structure and property, primarily when we are talking about highly crosslinked thermoset systems, and that is not limited to epoxies but of course is certainly characterized greatly by epoxy systems.

And, of course, in the industrial end of the game, the one in which many of you are involved, what we heard over and over was there is literally no time to back off and do the kinds of characterization in the structural property correlations that will be necessary in order to make the kind of predictions that some of these kinds of questions entail.

So, once again it was brought up, the necessity for this, and discussion of this type.

I guess the next point, and if I didn't say so before I'd like to say I will certainly invite all the members of my committee to submit their minority reports in full or in part when I finish these introductory remarks and we open the floor, because we had a pretty free-wheeling discussion over the brief period we had, and I'm afraid I won't do justice to much of the discussion in this short period; but I think the next important point that came up is that there is a fair amount, a fair body, of information about polymeric behavior which we can draw upon to be able to predict what kinds of properties we might have under a variety of these kinds of environmental and other conditions.

And I think John Halpin's description yesterday morning was to some extent an attempt to encapsulate what we presently know and put it into an overall framework; and I think within the limitations he described yesterday this works.

We do have an overall view of plasticization. We have a view of some viscoelastic properties of polymers and so forth. The problem once again, if you want to be specific, or if you wish to look at second-order effects, those which may have great importance over the long run but which don't show up in any great amount on any kind of short-term testing.

So we know a lot about polymer behavior. We know relatively little about specifics of the highly crosslinked thermoset systems and the second-order type effects.

There was a fair amount of discussion of whether we are talking about two types of water involved in the environmental response of epoxy resins, that is, that which is bound and hence probably plasticizing, and that which may be freed or in the bulk, which presumably would not be plasticizing, but may have other effects. Are there both kinds? If so, how much of each? This information, while it may be reasonably easy to ascertain, has generally not been obtained for most of the systems that we know about.

I think there was expressed a number of times the need for a more coordinated and a more extensive program in determining structural property correlations for the systems that we are dealing with, and once again it went back to the need for a well-characterized model resin system to deal with.

Now, primarily throughout all our discussions we were talking about the resin itself and maybe a step into talking about the fiber-resin interface, but by and large, the discussion was limited to the resins and not to composites in general.

It was our understanding that our committee was primarily talking about the parts of the problem, and that we'd expect Committee No. II to talk about how this can be integrated into an overall constitutive model.

So, I'm getting back at John now for getting me up here first.

Well, I don't want to go on in these general comments. There were a number of comments that had been made in terms

of what kind of techniques could be utilized, and I don't think I will take time to reiterate those here. For some of the committee who would like to discuss them specifically, I would welcome their comments as to what specific techniques could be utilized, and are being utilized, for that matter, to investigate these various effects.

Finally, the point was raised that there is a high probability of a variety of new resins coming down the pike in years to come, some of which may be epoxies and others which may be quite different, which will need the same kind of characterization, and that hopefully any kind of coordinated programs that are set up on this basis with epoxies could serve us in good stead for resins to come.

So, with those kinds of introductory remarks, I'd like to open the floor to one and all, any member of the committee, who would like to add some specifics that I obviously overlooked for lack of time, or maybe even lack understanding. I'd welcome those, or any comments from people in general.

Bill?

DR. JONES: Bill Jones, Air Force Materials Laboratory.

Just a question about a word, physical property correlation model. I just happened to look that up in the dictionary. Correlation literally translated means a very loose or a very weak association. May I recommend -

DR. GOLDFARB: More appropriate than we knew.

DR. JONES: Kind of in jest. But we have some pretty nice methods and I would really like to see some quantified, precise, exact measurements. Thank you.

DR. GOLDFARB: Your point is well taken, Bill, and of course the thing that came up within our group is that in order for that to be meaningful, that requirement for getting well-characterized clean resins loomed as the first order of business, because while we can get a lot of numbers of production materials, then the attempts to do that correlation, even by the dictionary definition of its looseness, is difficult.

Other questions? Comments? Objections?

Yes, sir.

DR. ROSEN: Walt Rosen of Materials Sciences.

We had a question in our group this morning about your question 5, and I bring that up in connection with the comment that Bill Jones just made.

How, or what is the answer to 5 or what are your suspicions and what impact would that have on the procedures that you would follow in making physical property correlation models?

DR. GOLDFARB: I think the general opinion of our group was that they didn't even want to talk about questions like 5 until we could better characterize. The suspicion was yes, there probably are all these things, all of the above or

none of the above, depending upon how you made it and what it is you made. And if you talk about it in abstraction it probably is not particularly meaningful.

I thought you were going to help me prepare my summary.

DR. BORSTELL: My name is Hans Borstell from Grumman and I'd like to make a point that may help Walter.

One of the things that has come out from some direct experience we have had is that the cure cycle used to gel the resin does have a significant effect on elevated temperature properties of composites.

Some of the data generated in the early days of 5505 Boron/Epoxy has shown that the type of cure cycle that we use has a very significant effect on the dry high temperature properties of the laminate. The study came about because we were trying to suppress an exotherm in thick parts. We had the opportunity to evaluate the various low temperature gelation steps before we went into the final 350°F cure and 375°F post cure. We found that if we jelled below 260°F, significant decrease in the high temperature properties occurred.

Due to stearic hinderance, we apparently lowered the crosslink density even though we post cured. Possibly certain types of curing mechanisms were occurring which were abnormal. Instead of reacting at preferred sites, we may have favored secondary reactions which modified the chain structure.

Since we have heard yesterday that bound water attached

to the unreacted sites is primarily responsible for the plastification and the swelling of the matrix, the way we cure the resin is critical to the moisture resistance of the laminate.

If you go one step further and post cure a properly jelled network, the cure reaction is driven even further to completion and less water pickup occurs as supported by test data presented yesterday.

DR. FOUNTAIN: I have got a slide here that shows a problem area associated with fabrication of the old NARMCO-5505 material with boron.

This slide shows the infrared spectrum of the caul plate and vacuum bag surfaces of a laminate after cure. The samples for the analyses were obtained by scraping the resin off the surface and forming a KBr micropellet. The resin is dicyandiamide cured so that the decrease in the nitrile absorption at 2200 cm^{-1} with the increase in the carbonyl absorption at 1720 cm^{-1} indicates the degree of cure. On the caul plate side complete cure is indicated by the absence of the nitrile peak and the large carbonyl peak. On the vacuum bag side, however, complete cure as indicated by IR is not apparent due to the nitrile absorption and the smaller C=O absorption. Thus on going from the caul plate side through to the laminate thickness to the vacuum bag side, there is a cure differential, and this may have a significant effect on the local mechanical properties and moisture absorption across the laminate's cross section.

Some data have indicated that the complete disappearance of the nitrile absorption is required in order to obtain the specific room temperature interlaminar shear properties.

DR. GOLDFARB: Thank you, Roger.

On the question of completeness of cure, we have in our laboratory taken a brief look at some of the resins that Dr. Levy looked at in their program on the effect of moisture, and in looking at the - what he called the STM - stress temperature and moisture resin, and comparing that with just the stress temperature one, there is some indication that the stress, even under stress and temperature, there was still some evidence of a little unreacted epoxy.

However, in the stress temperature and moisture, that unreacted epoxy was gone.

Now, the initial consideration was that, under the conditions of the moisture at the temperature and under stress, the material was being plasticized and an additional reaction could occur that could not occur otherwise.

In other words, we have reached the wet glass temperature of the system, and allowed further reaction.

This type of problem was brought up within our group about the question that within any thermosetting system there is a maximum glass temperature that could be obtained in the system if all unreacted groups reacted. But that in practice this is generally never achieved because the glass temperature of the system as it rises during cure reaches

the curing temperature and then the reaction stops, effectively; so that you always freeze in little unreacted groups.

And this is part of the uncertainty of the materials that you are dealing with that are dependent so much on the cure as well as on the original chemical composition.

Other questions?

DR. SCOLA: Dan Scola at United Technologies.

I just want to point out that to get around incomplete reaction of the epoxy system, you have to cure well above the Tg temperature. If the Tg is 300°F, I suggest you cure to 375°F or 400°F.

DR. GOLDFARB: That gets back to the post-cure comments that people make, I think.

Any other discussions? I'd like to thank all the members of my committee for their active participation in our discussions, and I know I got a lot out of it and I hope that the others in the group did, and that we somehow managed to convey some of that information to you here.

Thank you.

DR. VINSON: Thank you very much, Ivan.

For Group II, which is Characterization of Constitutive Properties, John Kardos of Washington University led that group. John.

2. Characterization of Constitutive Properties

DR. KARDOS: We followed our discussion outline (K-1)

CHARACTERIZATION OF CONSTITUTIVE PROPERTIES

Discussion Outline

1. How should the effects of water and temperature on the matrix properties be fed into a micromechanics model to predict stiffness, expansion strain and, perhaps, strength? What theoretical changes are needed in the present models? What property inputs will be needed? In the case of strength, does water exposure cause the interface to be a problem?
2. What kinds of mechanical tests should be used to characterize the thermal-water sensitivity in the unfilled matrix?
3. What kinds of uniaxial mechanical tests should be used to mechanically characterize unidirectional, continuous single-ply performance as a function of water and/or thermal exposure? Do we need a special test to look at the interface?
4. Do we need to carry out multiaxial mechanical tests? If so, what kind of test would be most sensitive to water?
5. Can we utilize the water thermal effect data from 3 and 4 to predict laminate properties? Does a format now exist which would accommodate the water-thermal environment effects?

reasonably closely with the exception of small deviations here and there. We started our discussion by splitting what we had to say into areas of first the matrix, secondly the fiber, and thirdly the combination of the fibers and matrix into a unidirectionally oriented ply. Finally we discussed the chemistry of the interface and the nature of other interface problems that would have to be examined to produce any kind of structure property predictive scheme for, in the ultimate case, a laminate.

We began by discussing whether or not Fick's Law was a reasonable thing to use for predicting moisture intake. The conclusion, generally I think, was that it's probably okay as long as you use it under conditions of constant temperature. And, on the other hand, if you knew how the temperature affected the diffusion coefficient, that problem could also be handled with available formats. Thus, in general we can handle the non-transient problem.

We also concluded, I think, that one can as well use concentration-dependent diffusion coefficients, if you know the nature of the dependency and that you can use this dependency in the format of Fick's Law with no problem.

When one has to account for temperature gradients and add transient effects, we can still do it in the format that's currently available, using Fick's Law, by the addition of the proper temperature coupling terms. So it seems in general that as long as we don't have to deal with a stress-coupled system, we can use Fick's Law quite adequately.

When we addressed the problem of stress coupling with diffusion, the consensus of the committee was that there really is no data available for water epoxy systems. There is some data dealing with other kinds of systems, other kinds of solvents in epoxy, where we have severe swelling stresses developing and so on, but there is little or no data in the area of water in epoxy, and that is something that really needs to be worked on.

We also concluded that one of the major things that should be examined with respect to the pure matrix was swelling and dimensional changes with respect to water, and that particularly we ought to look at how stress and moisture have to be dealt with in the case of crack propagation. That is, how does moisture affect crack propagation; particularly, what does it do to the so-called plastic zone out in front of the crack, and how does that in turn affect crack propagation through the pure matrix, and in turn, the fracture capability of the material.

We then spent some time discussing what kind of properties one should be measuring on the pure resin. One of these takes the form of a creep modulus response surface of the resin with respect to the log of the temperature on the X axis the log of time on the Y axis (3-D plot).

We also discussed how one would employ the time-temperature superposition principle to look at the response of the modulus to, first, different states of water and, secondly, different states of stress. Implicit in this

measurement the creep modulus or the shear modulus, is of course the glass transition measurement. Dr. Goldfarb has already discussed that in his presentation.

We also discussed the point that in order to do any of this kind of work, one has to know exactly what the curing history or the processing history was. If we don't do that, then we really cannot isolate the effects of moisture and temperature.

Next, we examined the measurement of the moisture effect on strength and we had a little bit of back and forth discussion on whether or not one needed to make biaxial measurements on the pure matrix. There was some opinion that one ought to characterize the biaxial failure modes for the pure matrix; but there were also other comments to the effect that if one did that, what good would it do you in predicting the properties of the composite.

It was also pointed out that when one tries to do time-temperature superpositioning with the kinds of matrix systems that we are dealing with, one has to be careful in terms of examining the temperature effects, particularly on a relaxation curve. One has to, in some cases, particularly below glass transition, correct the initial point on the curve for temperature effects.

We then got into a discussion of the composite, and for purposes of narrowing and focusing discussion, we kept our comments to the physical situation of fibers, unidirectionally oriented in a single ply. For a unidirectionally oriented

composite ply, the first item that came up there was that we absolutely have to know the void content; because if voids are present to complicate the situation, then we cannot expect useful results. Thus the first thing one ought to do in looking at the composite system is to determine whether or not you have a serious void problem.

Among other properties that were recommended for measurement was the swelling or dimensional stability; it was also pointed out that in this ply system we must account for anisotropic diffusion, that is, the diffusion is going to be different in the fiber direction than transverse to the fiber direction. And of course, when one must deal with bad interfaces and voids, then the anisotropic diffusion problem is compounded even more.

In the case of mechanical properties, we need the following property measurements for the ply material; the orthotropic elastic properties, the principle expansion coefficients or the swelling in the principle direction of ply, the principle diffusion coefficients, and the transverse shear and compressive strengths. Having these parameters, we can then formulate some kind of a micromechanics model to predict the ply mechanical response. All of these parameters of course, must be known as a function of temperature and moisture, so that we can produce a complete temperature-moisture response surface.

It was also pointed out that we need to look at uniaxial hysteresis experiments as a function of water and

temperature exposure for the ply and then move into the multi-axial stress-strain testing modes, probably sticking with the two-dimensional sheet type of specimen, in other words, maintaining the ply geometry. In this kind of composite ply we also have to consider the distribution of water in the plate. If you have a reasonably thick plate, it's very possible to have water concentrations that are high on the outside and low on the inside, or the other way around, if things are drying out. Thus it's possible that locally one can have high water concentrations in a position where the failure modes originate; and that of course, has to be accounted for. We also have to worry about local concentrations of water in high stress areas, namely at the interface; and once again that brought us to a discussion of the interface.

It was also pointed out that a good experiment to do would be to superimpose stresses on this individual ply in various ways while the system is exposed to the particular environment. One would then have the ply response for the temperature effects, moisture effects, and of course, the temperature, moisture and stress all superimposed.

The fiber problem came up again in our session. It was concluded that sodium and some of the other metal ions definitely were intrinsically present in the fiber surface. These ions were not inserted in the processing step and we will have to live with them in terms of about 2 to 5,000 parts per million, depending on the processing temperature. That being the case, we concluded that it was extremely important

to characterize the graphite materials particularly on the surfaces to see exactly what compositions we have to deal with in terms of metal ion concentrations.

It was also pointed out that sizing - in many cases epoxy, is used on graphite, particularly; and that we ought to know exactly what this sizing is before we can do anything with it, either live with it on the fiber or try in some way to get rid of it.

With regard to looking at the interface, the fiber and matrix ought to be characterized for their surface properties such as wettability. This ought to be done perhaps through a contact angle analysis. It was pointed out that this was extremely difficult to do with fiber, but that there are techniques, one of which is dipping a bundle of fibers in a particular liquid, to determine what the wettability and contact angle are.

We then discussed what one needed to do to characterize the interface in terms of how is it sensitizing the material to moisture. There was some argument among the committee about whether one ought to use a transverse tensile stress on a unidirectional ply or whether one ought to do some kind of a shear test, a short beam shear test or other shear test, to look at the interface integrity. Although I don't think we reached a clear conclusion, I think there were more people in favor of the transverse tensile test.

We discussed the problem of selective absorption of components of the epoxy recipe. Selective absorption of

these components on the interface could create totally different reactant stoichiometry during the cure cycle at the interface than out in the bulk. If that happens, one ought to know about it because it has a direct effect on the high temperature properties of the material. I think this phenomenon in fact could possibly be connected with the behavior that was mentioned by the gentleman from Grumman.

We then argued a little about whether or not a coupling agent was needed for graphite. The conclusion was that we do not need a coupling agent for graphite and that we ought to keep the graphite as clean as possible and not put anything else in the system to confuse the situation. The shear strength for graphite is adequately high now. It was pointed out that in fact it may be too high and a little bit of back-sliding on the shear strength wouldn't hurt, particularly in terms of toughness.

In light of looking at the chemistry of interaction at the interface and how it affects mechanical properties and also how water can affect the chemistry at the interface, we need to make wider and better use of some of the more sophisticated techniques that are now available, such as IR, Raman spectroscopy and so on.

We concluded that once we had the properties of the unidirectional lamina, an analysis of the laminate, which is made up of several of these plies, is currently feasible. That is, if one knows what the effect of moisture and temperature is on the individual ply, the format is currently

available for taking it into the laminate.

I think that summarizes the discussions. We are now open for questions at this point.

DR. HANAGUD: Hanagud, Georgia Tech. Could you elaborate on the last point concerning how you go to a laminate from a unidirectional composite?

DR. KARDOS: Dr. Pipes might wish to comment.

DR. PIPES: Thank you. One approach one could take would be to characterize the material, just as one does thermally, and look at equivalent coefficients of moisture expansion and then redo the problem in an analogous fashion to a thermal problem for laminated plates, and compute effective moisture moments and moment resultants and force resultants.

There is a standard technique which I guess most of us who have worked on laminate analysis are familiar with. I guess it can be attributed to Tsai and others, and we have just recently completed doing an analogous solution for moisture. I think the question that remains unanswered is how appropriate and exact that analysis is. It does not include the effects of stress upon moisture distribution, nor does it include transient thermal effects at the same time. In other words, we have just initially assumed a diffusion which takes place under isothermal conditions.

There are more problems that need to be solved, and I

think we are just beginning to scratch the surface of this area.

DR. KARDOS: It's certainly not a clearcut finished issue, but at least there is somewhat of a format there to start with.

DR. SCHAPERY: Dick Schapery, Texas A & M. With reference to Fick's Law, I believe you indicated in your summary remarks that we agreed that even with the temperature gradient one could use Ficke's Law?

DR. KARDOS: No. I indicated that with the temperature gradient we had to correct the coupling effect.

DR. SCHAPERY: So that the mass flow would be, say, proportional to the temperature gradient as well as the concentration gradient?

DR. KARDOS: Right. That's one possibility.

MR. WHITESIDE: Jim Whiteside, Grumman. I don't quite see when the coupling becomes important, because the diffusivity of the moisture is several orders of magnitude smaller than thermal diffusivity, and I am trying to think of the practical problem where Fick's Law doesn't work.

DR. KARDOS: Yes, the committee had the same argument. Would the principals in the argument care to go over that once again?

DR. SCHAPERY: Consider a specimen with a steady state temperature gradient, for example. The question is, can that gradient drive much through the specimen? It is not clear that the driving force of temperature gradient will produce significantly less diffusion of moisture than you get from a concentration gradient. The moisture diffusion due to the former gradient arises from an off diagonal term in the matrix of coefficient connecting moisture and thermal diffusions processes; and the only thing you can say about the off-diagonal coefficient is it's less than the geometric mean of the diagonal coefficient. However, it is not clear that the temperature gradient has a negligible effect.

I think the thing that can be said is that in many cases the thermal changes occur so rapidly that the problem can be treated as an isothermal problem.

DR. KARDOS: You mean isothermal in so far as you have set up a steady state gradient across the specimen because of having two surfaces at different temperatures.

DR. GOLDFARB: Ivan Goldfarb, AFML. I wonder in the consideration of diffusion if you are neglecting the approach to the glass temperature of the wet material, or is that covered by the temperature dependence of the diffusion coefficient?

I could well conceive, for example, of a diffusion front of rubbery material which would behave like diffusion at elevated temperatures even though at the ambient temperature.

DR. KARDOS: This discussion in the committee did not deal with that point at all. We considered that we were well below or well above the glass temperature.

DR. ROSEN: Walt Rosen, Materials Sciences. I would like to comment on the question of going from one level of approach to another with the knowledge of material properties. You addressed the question of going from layers to laminate, and yet in your presentation you identified as a more serious problem the need for determination of the properties of the layer. I think that it's fair to say that the analytical capabilities for going from constituents to layer is just as good as the analytical capability to go from layer to laminate. And although I think some remarks yesterday implied the contrary, I believe that there is a capability to take matrix diffusion coefficients or matrix swelling coefficients and predict laminate diffusion and swelling coefficients; to take matrix and fiber thermal conductivities and predict unidirectional conductivities, etc.

Was that controversial or did I get something wrong?

DR. KARDOS: No, I don't think that was controversial. I think in the case of stiffness and strength that there was general agreement that one could draw those conclusions as you stated them.

DR. ROSEN: I mean in the case of swelling coefficients and thermal conductivities as well.

DR. KARDOS: We didn't discuss the thermal conductivity problem at all, but I think a comment might be in order here.

DR. WEITSMAN: In my opinion it is worthwhile to investigate the question of moisture diffusion along the interfaces between fibers and matrix. At the present time it is not obvious that the absorption characteristics of the composite are inherently the same as those of the neat resin and of the fibers taken separately, and that no new features are caused by the interfaces. This question could be resolved by suitable experiments.

DR. KARDOS: Our discussion of the calculation of the ply properties with respect to diffusion was limited to the situation where we had "the perfect interface and no voids", and as soon as you get away from that situation we can no longer predict properties.

DR. ROSEN: Yes, I think I'm suggesting that maybe the problem is one of trying to establish some correlation or lack thereof between the simple models that one would be able to use today and the experimental data that do exist. I wanted to make a second comment relative to your suggestion that interface strength be measured by a short beam shear test: Please don't.

DR. KARDOS: I thought you might be worried about that point. We also discussed it in the committee.

DR. ROSEN: Seriously, I think that a short beam shear test, in addition to all its other shortcomings, which have been discussed adequately in the past, takes on another problem here. When you are looking at environmental effects, the matrix stiffness properties change at the same time that the interface changes, and those two effects cannot readily be segregated in a short beam shear test.

DR. KARDOS: Do you have your own preference?

DR. ROSEN: Well, my preference for a shear measurement is a plus and minus forty-five degree coupon. It has its shortcomings, but I think it's by far the best available test specimen.

DR. CROSSMAN: Frank Crossman, Lockheed, Palo Alto Research Laboratory.

I want to address something that Walt Rosen brought up; and that is the ability to calculate from the fiber and matrix properties the lamina and laminate properties. I have just heard a seminar recently by George Springer of Michigan working on an AFML contract, who did exactly this.

He measured moisture diffusion rates on epoxies, as well as unidirectional laminates of T-300/934 and crossplied laminates. Of course you realize that there is going to be a considerable difference in the internal stresses in the laminates compared to the neat epoxy.

He found no influence of these internal stresses on

the diffusion coefficients, so at least here is some evidence to indicate that maybe stress isn't that important in affecting the rates of diffusion through the material.

Maybe someone from AFML might want to comment on that.

DR. KARDOS: Are there any other comments on that point? Ken?

DR. KIBLER: Kibler, General Dynamics. Not exactly that point, but a related point. You talk about the need for swelling measurements and for anisotropic diffusion coefficients. I think that the combination of the Shen-Springer data, which Frank just referred to, and all the GD data, which we've just partially started to disseminate, contains all the necessary measurements.

Does anyone have any data which indicates there is any kind of wicking effects along the interface?

We don't have any. All of our crossplied laminate data I think can be accounted for in terms of the work in Springer and Shen's paper by just accounting for how the fibers are oriented and what effect that has on diffusion in different directions.

I don't think there is anything mysterious, and we certainly don't see anything that looks like preferential wicking along fiber directions. I think all the measurements are there.

DR. KARDOS: There were some data presented yesterday

that indicated that there might be wicking. Obviously, if you have a poorly fabricated system, you certainly can have wicking. If you also use high post-curing cycles and then come down to performance temperature, the stresses can rise high enough so that microcracking at the interface occurs. Anomalous diffusion then occurs along that interface. I'm not sure you can consider it wicking. I suppose it would be.

Larry Nilson and Paul Peyser of Monsanto showed this some years back.

DR. KIBLER: First of all, we only use well-manufactured specimens at General Dynamics.

DR. KARDOS: Obviously

DR. KIBLER: But I will certainly agree with your point.

DR. KARDOS: You and Max Waddoups must be in the same club.

DR. KIBLER: He told me to say that.

DR. KARDOS: We just brought it up as a point that one ought to consider.

DR. ROSEN: May I just add to that, there was some discussion in our group that thermal spikes could change the situation that Ken was just talking about, and I guess that's what you were alluding to, namely that you might open up

some of the cracks and therefore get a departure.

DR. KARDOS: It looks like everybody's ready for lunch.

DR. VINSON: Before everybody leaves there are two items to bring up. One is that we have a complete list of attendees available that is incomplete only in the sense that all of the University of Delaware people, Vinson, Pipes, Daugherty, McCullough, were not included.

The second thing is our Department of Continuing Education would very much like for you to fill out a very brief form so that they can evaluate this program held here.

LUNCHEON RECESS

DR. VINSON: Gentlemen, we will now resume. The session chairman for this afternoon is Dick Daugherty who is the Assistant Dean of Engineering here, also, an assistant professor in Mechanical and Aerospace Engineering and also who is a member of our Center for Composite Materials. So I will turn the mike over to Dick.

3. Failure Processes

DR. DAUGHERTY: We will continue then with the group reports and discussion. Group 3, Failure Processes, was chaired by Walt Rosen, of Materials Sciences Corporation.

DR. ROSEN: The subject of failure processes is one that we concluded was among the more difficult problem areas. Our objective was to try to establish some definition of critical issues. I don't know that we were as successful at that as we would have liked to have been, but I do want to lead you through some of the discussion that we had.

If I may have the first slide. (R-1) We viewed one of the objectives of this workshop to be an attempt to bring together people who are studying the failure process at different levels and we felt that somehow we needed to establish a consistency that would enable us to go between the different levels of approaches shown here; that is, to translate our understanding of constituents into an understanding of unidirectional composites, unidirectional composites to laminates, structural elements, and structures.

We probed around a little bit, attacking this problem from two different directions, basically starting at

FAILURE PROCESSES

Level of Approach:

Constituents
Uni Composites
Laminates
Structural Elements
Structures

the top of the list and working down, and then at the bottom of the list and working up; and I think we were much more successful with the second approach than the first approach.

That procedure will be the format of my summary to you of our discussion. We postulated that a representative problem at the structural element level is a composite laminate with a hole in it subjected to fatigue loading in the presence of a variable temperature and moisture environment. We said that if we could get an understanding of the influence of temperature and moisture upon performance of that laminate, where performance means failure and lifetime and reliability, that if we could get that understanding, we would have accomplished our objective. Over the long run, and therefore, for the purposes of this workshop, we would like to identify the critical issues that pace us in our development of that understanding.

Next view graph, please. (R-2)

So we said, "Okay, what exactly are the methods of analysis that the structural designer is going to use? What is the information necessary in order to be able to utilize these methods of analysis?" Hopefully those answers would lead us to some identification of shortcomings.

At this point we are going through the levels of approach from the bottom of the list up, so that we start with a structure and we assume we know all the properties of the materials from which that structure is fabricated, and

METHODS OF ANALYSIS

Stress Distribution
Laminate Analysis
Layer "Failure" Criteria
Initiation of Damage
Propagation of Damage
Failure

PROPERTY PREDICTIONS

Moisture Diffusivity
Swelling Coefficient
Thermal Diffusivity
Expansion Coefficient
Conductivity
Moduli

the first analysis job is to get a stress distribution. If we have a stress distribution we need to be able to perform an adequate laminate analysis at a point. When we have our laminate analysis, we know what is going on in the layers, and we need to know what causes layer failure, - whatever we might mean by failure. Perhaps we should ask what it is that causes initiation of damage; and how does the damage that has initiated propagate in order to bring about failure?

The task of failure prediction has two parts: What are the local values of the state variables, namely stresses, temperature, moisture content, et cetera; and what combination of those state variables produce failure? Thus, to a certain degree, we overlapped the work of the previous panel in our discussion of how does one predict stresses. In view of some of the discussion after John's presentation this morning, I'd like to make some comments and to make clear to you the viewpoint that was taken by our panel because I suspect that it's controversial. If not, fine, but if it is, I'd like to get some reaction to it.

The committee believes that if we have to utilize a laminate analysis, that there is a good capability for property prediction. Given the following constituent properties: the moisture diffusivity, the swelling coefficient, the thermal diffusivity, the expansion coefficient, the thermal conductivity, (or for that matter the electrical conductivity) the elastic constants, or the viscoelastic constants; if we know all of these properties for the constituents.

under the assumption that the interface is a perfect interface, we can compute all of these properties from existing mathematical material models for unidirectional materials. Further, if we know them for unidirectional materials, we can predict them for laminates, and we can then solve the diffusivity-temperature-stress problem for general laminates subject to certain restrictions. Thus, we can solve them very well if the moisture diffusivity is independent of temperature and stress and if the thermal diffusivity is independent of moisture and stress. If those conditions are not satisfied, then you lose a little bit of your capability. And finally, when you get down to non-linear behavior, then you have problems for which our capability is much more restricted.

Basically our conclusion was that when it comes to this type of an analysis of a laminate, the limitations are not a critical issue. That is, there may be deficiencies, but this is not where the critical problem lies.

Next view graph please. (R-3)

The problem does lie in a definition of what the failure modes are, and the failure modes have to be defined at several different levels. On the macro level - the one that most of the discussion has been centered on - there is the question of strength, or fracture. There is some lack of clarity as to what we mean by these words, because static failure, in the practical case in which there is a

FAILURE MODESMacro

Strength/Fracture

Residual Str./Lifetime

Stiffness

Local

Long. Comp.

Long. Shear

Trans. Strength

Long. Tension

Interactions

Micro

Matrix Cracks

Change in Matrix σ - ϵ

Chemical Effects (not disc.)

Interface Degradation

notch or a stress raiser present, is partly a case of local material strength and partly of propagation of damage. This might be called fracture, although of course it's very different from fracture in a homogeneous material.

The problem area that we felt was more important was the question of failure in the sense of reaching the limit of lifetime, which really means that we are then talking about the residual strength properties after some exposure to temperature and stress. Also something we didn't talk about much this morning are other macro failure criteria such as stiffness limitations; both initial stiffness and residual stiffness. These apply to vibration problems, to structural design problems which are deflection limited and to buckling problems. In all of those cases, stiffness is important, and perhaps of greater significance in the presence of moisture.

On the next level down then, we say that our requirements are for definition of those failure modes in unidirectional materials, which are sensitive to matrix properties and therefore sensitive to moisture and temperature. I should emphasize that this discussion is based on the concept that we are talking about influence of moisture and temperature, and from that, one would infer that if you dropped the influence of temperature and moisture out of the problem, that you would know all the answers. Unfortunately, particularly when we talk about things like lifetime and residual

performance capability for both strength and stiffness, our understanding is incomplete even in the absence of environmental effects. That fact complicated our discussion.

At any rate, the longitudinal compression strength of a unidirectional material is certainly something that is important and very sensitive to matrix properties. There have been observations in static loading cases of a change in failure mode from tensile fracture to a micro instability in compression as a result of the presence of moisture and temperature. The importance of the longitudinal shear and transverse strength is obvious. Environment has a less direct effect upon longitudinal tension behavior, but perhaps an important effect when one considers interactions among the various stress components.

This brings us to the question of micro failure criteria that need to be addressed and understood. These include accumulation of cracks in the matrix, influence of moisture in changing the matrix stress-strain characteristics, plasticization, chemical effects, et cetera. We took the view that for certain of these effects (and chemical effects are representative) someone is going to have to tell the structural designer what the constitutive relations of the material are as the result of some specified environmental exposure. To the degree that the effect is just a change in magnitude of properties, then that's something that the analysis methods could easily cope with.

Interface degradation is something we don't understand. We don't know whether it exists or not. We do know that if there is substantial interface degradation, it can have an important effect, particularly on something like the longitudinal compression.

Those are the subjects we discussed, and there should logically follow from that a long list of critical issues, and that second phase of the presentation is much less complete than we would like it to be, but the following reflects some significant things that we were able to discuss.

(R-4) We discussed this question of the adequacy of the analysis methods, particularly when you were talking about stress distributions around the hole, for example. One knows that under fatigue loading you would get some material degradation, particularly in the presence of moisture and temperature; therefore, there would be some redistribution of stresses, and our capability to predict that might or might not be adequate. The important point was that the adequacy of the analysis methods depends upon your requirements for your accuracy. Your requirements for accuracy depend upon knowing the failure modes. So that as long as there is uncertainty about what failure modes may arise due to environmental effects, we can't resolve the question of whether the accuracy is good enough, and therefore the question of whether or not the methods are adequate.

ISSUES

1. Adequacy of Analysis Methods

Accuracy

Failure Modes

Approach

Identify modes in uni. comp.

Hypothesize micro causes

Test hypotheses

2. Time Dependent Effects

Temperature

Moisture

Stress

∴ Time

Important for Cure and Residual Stress

3. Physical Causes for Observed Phenomena

4. Accelerated Test Methods

The approach that we recommend is to work down from macro to micro as engineers in the simplest possible way; to go through the existing analysis methods; to get down to a unidirectional composite; to identify some tests that can be performed in order to observe failure modes in the presence of environmental degradation. For example, treat the problem of a unidirectional composite with a hole in it subjected to either static or fatigue loads in different directions. When we see what these resulting failure modes are, we may hypothesize micro causes. We may then ask what possible behavior of constituents or interface might account for the physically observed phenomena in these tests? Then we have a motivation for doing the study of individual constituents, where the motivation has been generated from above, and what we are really doing is testing our hypotheses by evaluating the performance of these materials.

We had a fair amount of discussion about the issue of time dependent effects and basically the thrust of the discussion was that if you have temperature and you have moisture and you have stress as parameters that are of importance, it's not unreasonable to expect that time is going to be a parameter of importance. Some calculations have been made, and there have been some experimental observations, that support the fact that when you are fabricating these composites, these time dependent stresses can change quite a bit with changes in environment, such as cure rate, for

example. The residual stresses that result from the curing process are important in composites. Therefore, we know that treatment, for example, of viscoelastic behavior of a laminate is going to have importance at least for assessment of the fabrication problem. There is some lack of unanimity in our view as to how important it is beyond that and testing will be necessary in order to give us some insight into that problem.

And finally, one item which pertains throughout is the physical causes for observed phenomena. As mechanicians as mechanics of materials people, we have to turn to the chemist and say that we need to understand what it is what is causing the change in properties.

When we get a change in the stress-strain curve, is it just that there has been some chemical interaction that has caused this change or is it that there is some micro cracking, because the difference between these two things may determine whether it's just an influence upon stress-strain characteristics or whether it's something that would go beyond that and impact the failure prediction as well.

I have tried to summarize for you what we discussed this morning. I will welcome some discussion. I count on my panel members to help in the discussion.

MR. JONES: Bill Jones, Air Force Materials Lab.

With regard to the failure modes, and the next view graph relating to kinetics or the time dependence, I would like to add my voice to the side that was for including or incorporating the time effects. And just in order to emphasize the point, perhaps we can recognize that time can be listed three or four times. The time which represents the age of the component, the time of exposure to the various environments, e.g. airframe log time. And then certainly the time as representing the duration of that particular load cycle that is being investigated at a particular moment.

Time plays a very important role when we consider materials "with memory", and there are all sorts of implications that come about. We need to quantify, or approximate as best as we can, each time dependent phenomena, and then perhaps we could prioritize the significance of each of these things if we are talking about, for example, crack growth in a time-dependent material, that is also plasticized by a diffusing media, it's of interest to know whether the crack grows at furlongs per fortnight or angstroms per century.

And we must recognize in both the total range of mechanical characterization and the failure criteria evolution that the locus and the mode of failure might well change at different extremes in our operational regime. For example, the cold dynamic tests will fail substantially different than the hot, wet, creep.

Question from the floor not recorded.

DR. ROSEN: I'd like to interrupt you there just for a second. First of all, I have to apologize to the panel because you have identified something that we did talk about, which I did not report; namely, that by understanding the time dependent properties we will perhaps get some guidance in accelerated test methods.

Also, I would like to emphasize that we have no assurance that the failure modes that we interrogate by our tests at the early stage of lifetime, will be the failure modes that are the driving ones at the critical point in lifetime. I believe that that is one of the critical issues we face. The panel was very concerned about our capability to obtain high reliability for our designs. I thank you very much for those comments.

If there are no further questions, I wish to direct some comments to Dr. Francis.

The statement I made during this presentation was that if we assumed that we had two phases that were well bonded and if we had all of these properties for the constituents: moisture, thermal or electrical conductivity, elastic or viscoelastic moduli; if we were dealing with linear problems; and that if moisture diffusivity is independent of temperature and stress, and if thermal diffusivity is independent of moisture and stress; that we could go from constituents to laminates and predict all of these properties for

the laminates. Also that we could solve the problem of temperature stress and moisture content in a laminate. Our group felt that, although there were questions associated with the analysis capability, such as perhaps it is non-linear, or perhaps the moisture diffusivity and the thermal diffusivity are each dependent upon the other respective state variable, and therefore it is a strongly coupled problem, perhaps, that with those exceptions that we felt that the analysis methods were in pretty good shape and therefore, in focusing on failure prediction we would not be motivated to describe the stress analysis aspect as a critical issue.

I am asking you for your reaction and if you agree with that or not.

DR. KARASZ: I'd like to comment on that. To reiterate what Ivan Goldfarb said this morning and to emphasize it, that is just what you can't assume, that there isn't a change in the state as the moisture transfuses in. If there were, we wouldn't be here because moisture diffusing into a rubbery state would be relatively unimportant. Moisture diffusing into a glassy state would be relatively important. It's the fact that there is a front or change of status actually that's causing a problem, as I understand the problem that we are addressing ourselves to.

So this is a thing that you cannot assume, it seems to me.

DR. FRANCIS: Let me just make one little comment on that. I'm prepared to believe that we can probably take the properties that you described here for the ply and adapt them to a reasonably accurate working method for constitutive behavior of a laminate, but when it comes to failure prediction, then I'm a little bit skeptical about whether or not we can do that in failure.

DR. ROSEN: I will agree with that.

DR. PIPES: I'd like to make a comment, Paul.

Byron Pipes, University of Delaware

We talked a bit about anisotropic diffusion, and I'm curious if anyone has any idea how we -- if and when we are able to describe that phenomena -- how we will use it. I have difficulty visualizing the boundary value problem which we will solve with anisotropic diffusion.

Anyone want to speak to that?

MR. BROWNE: Jim Browne, Rockwell International

Anisotropic diffusion is really quite easy to deal with. We at Rockwell developed a simple method of determining the three diffusion constants you find in any composite material, and it's really quite easy to describe anisotropic diffusion with a three-dimensional finite difference solution to Fick's Law.

Dr. Francis had a good form of that yesterday afternoon. You find on a real par though that the other two

diffusion constants on your edge aren't very --

DR. ROSEN: I thought that was Professor Pipes' point, wasn't it?

DR. PIPES: Exactly.

DR. ROSEN: In a common boundary problem it's going to be one-dimensional diffusion.

MR. BROWNE: One-dimensional except on your edge and holes it's extremely important. So I'm really not willing, because of the bolt holes alone, to say the other two diffusion constants aren't important. Attachments for composites is extremely important.

DR. PIPES: I don't think we should ignore Professor Karasz's point. I'd like perhaps someone to comment on that, namely what is the importance.

DR. ROSEN: I believe the question is: how do we perform the stress analysis state in a laminate in which we have temperatures that are on both sides of the glass transition temperature? Is that correct?

DR. KARASZ: Exactly, yes.

MR. WALKER: I think, Walt, when you showed in your micro slide up there -- this is matrix cracking and chemical effects, the environmental degradation. It's our

concern precisely over the role that the interface and the change of state variables play in trying to incorporate that kind of behavior into failure predictions. And it's where I see the predominance of this effect has to be of concern. Otherwise you are going to miss.

DR. ROSEN: Joe?

DR. AUGL: I'm not sure whether I understood the question right. If we talk about these resin systems for high performance composites such as 5208 and 3501, we actually never go through the glass transition temperature. The performance temperature, which we are concerned about here, is at the most 350°F. This is always lower than the glass transition temperature, even for the moisture-loaded resins.

(Cries of no, no, no.)

DR. BASCOM: Will you please amplify their answer.

DR. AUGL: I have rigidity and damping data out in my car at least those I have measured on 5208 and 3501. I don't know how you measured the glass transition temperature. However, if one determines it from the maximum of the damping curve or from the intersection of the horizontal and the steep part of the modulus curve then one finds that neither is lower than 350°F. Except you refer to the micro zones; I would not know how to determine the Tg of those.

DR. ROSEN: That's Dr. Augl of the Naval Surface Weapons Center, by the way.

Did you want to respond to that? Let's stay on this subject.

DR. KARASZ: Okay. I have only been going by what has been said yesterday, but it seems to be obvious that the concentration gradients here, and there must be local regions which are below the T_g , that would be one point. The second point was also one that was made yesterday, the T_g , especially as far as mechanical merits are concerned, is a very wide zone. We may be just entering it, and since we are talking about factors of two or three or four in terms of mechanical properties, not orders of magnitude. As we go right through the T_g , the modulus drops by factors of about two or three or four. We are very far from that. Otherwise the wings would have fallen off by this time or would have blown away, not even fallen off.

So we may be just entering the beginning of the zone, and that alone is enough to bring us all here apparently.

DR. AUGL: I agree with you there because we also have observed that the modulus curve, the horizontal part, drops down in absolute values, even way below glass transition temperature. This is true. The total curve of modulus versus temperature is dropped down, although the glass transition temperature is still above 350°F.

DR. KULKARNI: Dr. Kulkarni, from Materials Sciences Corporation

I have a comment to make. You did not discuss adhesive failure. Was that downplayed in your panel?

DR. ROSEN: No. When we started we said that we would select a structural element as being a representative problem and we specifically discussed adhesive bonding as an alternate to the problem of the laminate with the bolt hole in it, and we decided that the philosophy of what we would recommend would be the same for one as for the other.

DR. GOLDFARB: Goldfarb, AFML. I was waiting for somebody else to get up and talk about Tg data, but it's my understanding that there are, and I have seen some, data to indicate that there are Tg's in moisture-laden systems that get down below 300 Fahrenheit for systems that we have been describing here these last couple of days.

DR. ROSEN: With what curing temperatures for the system?

DR. GOLDFARB: With standard cure, post-cure. You get them -- the so-called maximum seven percent moisture of a resin, moisture absorption, I believe, gets our Tg down below 300 Fahrenheit. Maybe somebody's got some data that can corroborate that. I don't have the data with me and I can't recall, but it seemed to me it was something slightly below 300 F.

DR. ROSEN: Let's keep open the option that the structural designer is going to come to you and insist that you find a post-cure that raises the Tg a little bit.

DR. GOLDFARB: This is wet now.

DR. ROSEN: I understand. But, if you drive it up prior to moisture by post-cure, wouldn't you expect that the change due to moisture would not be as substantial?

DR. GOLDFARB: My prediction would be that the change would be just as drastic, it would just be all moved up a little bit, it would be shifted.

DR. ROSEN: That's all we want.

DR. GOLDFARB: If you move your dry Tg from 350 to 400, then you may move your wet Tg from 300 to 350.

DR. ROSEN: The point is that the problem might vanish if you do that.

Jim?

MR. WHITESIDE: Jim Whiteside of Grumman.

What the designer wants, obviously, is a material whose Tg is well clear of its application temperature for the humidity it's going to see in service. It's as simple as that. If you are going to exceed Tg for any time of consequence you just can't get away with it.

The systems have to be fixed, or the application is limited.

DR. ROSEN: Bill?

MR. WALKER: Bill Walker. That's true. But today's designer is looking to 220, 250. Tomorrow's designer is looking at 350, and no telling where the day after tomorrow. That's why we are here.

DR. AUGL: Again, I think I have said this several times, T_g alone is not enough. You can be way below T_g and you already lose strength in the composite. What all the real reasons may be for such behavior I don't want to argue. One of the reasons however, is, that moisture reduces the matrix modulus. Compare the wet modulus, and the dry modulus curves then you see the difference even way below T_g . The loss in modulus goes almost down to room temperature. At 100°C it is already quite pronounced. At this temperature you are way below glass transition temperature. Therefore, glass transition temperature alone doesn't tell you anything. The performance temperature has to be obviously below glass transition temperature.

I agree on that. But that is not enough.

DR. ROSEN: I think the points that we are discussing should be separated into three parts:

We are going to have to be able to cope with problems associated with going through the glass transition temperature, I believe, in order to understand what is happening during the fabrication process. That's part one. Part two is that even if we always operate below the glass transition temperature, we have to be concerned with moisture and temperature effects, because there are property changes which may be important. The third aspect which Jim Whiteside and I are suggesting, is that from the point of view of a practical design, there is going to be very heavy pressure to have a materials system which enables us to have an operational envelope below the T_g . Structures people are suspicious about hysteresis loops and the like, that are going to be associated with crossing the T_g . These could create additional failure modes that we would like to stay away from. If that is not possible, then, we will worry about the next line of defense.

DR. GILLHAM: John Gillham, Princeton University.

Aren't we also worried about the transitions of the

water itself? What happens to water-laden laminates, on passing 0° and 100° Centigrade? These questions haven't been answered either.

DR. ROSEN: Yes. And in fact I think the evidence that thermal spikes have caused some micro cracking, or something that has increased the moisture absorption of the material, also has implicit in it that a freezing cycle would permanently aggravate the material.

DR. DAUGHERTY: Thank you all.

The next leader is Byron Pipes for the group for Test Methods and Experimental Research.

4. Test Methods and Experimental Research

DR. PIPES: First I'd like to start this presentation by saying that Ken Hofer, who was originally scheduled to host this session, was unexpectedly unable to be here due to a death in his family. Therefore, I happily took the position, test methods being something of my interest anyway.

In our group we had twelve active members besides myself: Eugene Sincich from Stanford Research Institute, Hugh Gibbs from DuPont, Richard DeIasi from Grumman, Maurice Silvergleit from David Taylor R & D Center, Don Adams from the University of Wyoming, Bob Richey from the Naval Air Development Center, Ed Deska from the Naval Air Development Center, A. Mazor from Illinois Institute of Technology, Paul McMahon from Celanese, Joe Leal from Celanese, Jack Reynolds from General Dynamics and Bob Carlson from Georgia Tech.

I'd like to say that our group strived to solve a more pragmatic problem, namely how does one test for these phenomena, and to that end we are going to make some recommendations to you, some of which may not seem pleasing to you from an aesthetic point of view, but nevertheless we must in some of our acceptance testing, et cetera, use low-cost short-time duration-type testing in order to be able to work within the economics of the situation.

We divided our activities into four specific areas and set goals for ourselves, namely in developing test methods which are required in resin matrix synthesis for moisture resistance.

In addition to that, we believe that once a resin has been synthesized and it appears to be a candidate for composite material applications. We believe that there needs to be some quality control, quality assurance-type test methods which the vendor and/or the user can exercise in each batch of material.

We have seen wide variations in the properties of these materials, batch to batch, and therefore we must exercise some quality control.

And this is not unique to the moisture problem. It's just another of the areas that must be considered.

The third area is that of design data and therefore we must develop test methods to produce design data for,

after all, it is the designer who has to use this information in configuring structural components for either airframe or propulsion systems. And therefore the test methods must yield design data which can be used by the designer.

Finally, we looked at the problem of service qualification tests and test methodology, and I think that in all of these cases we may have given more of a broad brush investigation. We felt, I think, in two hours that we could have spent two weeks on any one of these topics and probably should in the future. Nevertheless, we did make some recommendations, and I'd like to summarize our results.

First of all, test methods for resin synthesis and for assessment of moisture sensitivity. We discussed briefly our interest in looking at neat resin systems and we had in our group a large number of material producers. We had Hercules represented. We had Celanese represented. We had DuPont represented; and therefore we did have a good deal of input from the synthesis people.

There was some discussion as to whether or not we should do neat resin tests at all. The conclusion was that yes, some neat resin tests need to be done in the early stages of a resin synthesis program, but that we have very little confidence, many of us, that the neat resin properties can be translated to the composite properties. We hope we are wrong, but nevertheless we have some question in this regard.

Now, what test methods do we recommend that one conduct in a neat system? Basically you could guess them. We can recommend that you look at the T_g , the glass transition temperature of the matrix; we recommend that you look at the swell properties, the coefficient of moisture expansion. We recommend that a standardized test geometry and test condition be developed and that we all follow that to some extent, if possible.

And here I call on A.S.T.M. to begin actively pursuing this problem. Many of us here are in fact members of their Fibrous Composites Committee of A.S.T.M., and I think you will see some activity there, hopefully, in the not too distant future. But it's been my experience, in spite of the fact that I am an A.S.T.M. member and am fond of the conferences, that the lag time between need for a test method and certification or standardization of that test method is many years. In fact, by the time the test method is developed in many cases we are on to another problem, and it's really not of much interest to us any more.

Leaving neat resin systems, we recommend that when a composite is configured of the new candidate resin system, that a large number of tests be performed. We recommend the interlaminar shear test, (A.S.T.M. D344). We recommend, again, the glass transition temperature test. In addition to the interlaminar shear test, we recommend an inplane shear test using a plus-minus 45 degree tensile

coupon. We recommend a zero degree flex test. We recommend that the coefficients of moisture expansion and of thermal expansion be measured. And finally we recommend that a study be undertaken to determine the sensitivity of the results of these various tests to moisture, to the presence of moisture and its deleterious effects to the composite system.

In fact, the question was raised by the materials producer, if we run all these tests and we get Material A and Material B, which do we tell management is a good candidate for our new product line?

Since the answer to that question is very difficult, it can only be solved by a university consultant!

Seriously, it is a difficult question, and therein lies our reasoning for recommending that a round robin sensitivity test program be undertaken and sponsored naturally by the Air Force.

We further recommend that sample conditioning standardization be undertaken, such that we avoid any artificial damage of the material.

If micro cracking is an artifact of water boil and is not truly the result of long-term exposure, then it should be precluded from test programs. Finally, we recommend that a uniform moisture profile be attempted in all test specimens, since it is well known that a simple weight ratio of moisture is not adequate in describing the state of moisture within the test specimen.

Number two, we proceeded to ask the question what tests would be conducted once we have achieved a candidate material or resin system.

And the answer that we proposed was not a very happy one, I think, but indeed we have to conduct some tests on prepregs. Currently A.S.T.M. is recommending some standards for gel time, flow, and percent volatiles in a prepreg system.

We have not solved the problem as to whether or not we should go directly to a cured laminate or whether or not we should in fact focus on the pre-cured material. I personally lean toward the former, the completely cured laminate exposed in a given standardized conditioning system.

We therefore recommend that for quality control tests, that all the proposed tests be performed in order to analyze candidate resin systems and they also be performed as quality control tests.

Probably one of the most significant needs we have today, I think, is to assess how much our design data really changes, based on the presence of moisture in our composite material. Therefore, we are recommending exactly what Dr. Rosen recommended, that the elastic properties of the lamina now be characterized, the coefficients of thermal expansion and moisture expansion, that the properties of the composite

which are sensitive to moisture -- I am talking now of the composite lamina, namely the transverse modulus, the transverse ultimate strain, and the transverse ultimate strength, inplane shear modulus, inplane shear strength and the compressive properties of the lamina.

While we have some reservations that modulus will change, we do recommend that we measure compressive modulus until we are sure that it does not change. In addition to that, ultimate compressive strain in the longitudinal direction and ultimate compressive stress and fatigue properties, particularly compressive fatigue be studied. There was some discussion about developing creep data for these materials in the presence of moisture, some counterarguments, since we do not generally see a great deal of creep in fiber dominated laminates, there.

One of the most insidious areas, I think, in composite analysis, will be joints, and adhesive joints will possibly be the most difficult to characterize for design data in the presence of moisture.

But we also feel that there is some change in behavior of bolted joint applications due to moisture, and therefore we need design data in these areas as well.

It could well be that adhesive joint behavior will look very much like the resin-dominated properties of the composite. Well, the last area that we chose to look at was test methods for service qualification. This is a very

important area. NASA and FAA, as well as Air Force, are currently struggling with this problem. They have flight critical components which must be service qualified, and the question arises -- many questions arise really -- as to how in fact do we do service qualification tests which include moisture effects.

We first dealt with real time load environments, including temperature and moisture. We believe that a commitment should be made in this area and that the long term exposure data must be generated. When we say long term we are talking about years, ten years probably.

I heard the comment recently that if we don't start now, ten years from now we won't have ten-year data. I think that that's an understatement, and we in fact must start doing some real time testing. I know that the Navy is actively doing this. I do not know what the Air Force has planned in this area.

Well, the point that I am trying to make here is that if we don't get real time information and we do only accelerated testing, we will never know how accelerated testing relates to real time testing, which is the real issue in this area.

But what are some of the problems? The problems which must be solved in real time include definitions of the environment spectrum. Although I can foresee that that is a fairly simple system to design, it will not necessarily be

easy to implement. Strain instrumentation or behavioral instrumentation, in the environment seems to be a difficult area. And I think that someone has to stop now and address that problem.

We don't seem to be able, in the case of electrical resistant strain gauges, to keep these gauges on the structure in an accelerated environment, and possibly not in a long time environment. So that problem must be solved. Otherwise we will never take data continuously over the life of the structure.

I had an aircraft company come to us recently (the company will go unnamed) to discuss using strain gauges in flying composite components. The conclusion of the discussion was that the persons involved didn't understand the strain gauge results, and therefore no flight components would be strain gauged. I think that is an unfortunate position and we cannot be forced into that position with moisture.

In the case of accelerated testing, we must learn how to superimpose the combined effects of temperature and moisture in order to be able to define accelerated spectra, and I think we have talked about that.

Certainly Dr. Rosen addresses that fact with the time dependence of the material properties. In accelerated testing we must insure that no localized effects control strength; that is to say, localized effects which would not be present in a real time environment. And I think that is the concern

we as testers have, that we not subject these composite structures to water boil or to artificial environments which result in localized failures which precipitate failure of the component.

When we compared constant amplitude fatigue tests to what we have now, in random spectra for fatigue analysis for fatigue simulation, we reminded ourselves that for quite some time, we have used Miner's rule for cumulative fatigue, knowing all the while that it was at best a first order approximation.

Again, we see that strain instrumentation and test methods for accelerated testing is a difficult problem that's not yet solved, and that someone needs to address. In testing we must continue to understand the action of moisture diffusion so that we can realize that when a structural component has a large moisture gradient it is not fully saturated and that our test time frames must be a function of diffusion rate.

Finally, we address the problem which we started out with basically, that unless we understand the relationship between accelerated testing and real time testing, there is no sense in doing accelerated testing. And yet our budgets will force us to accelerated testing, and therefore accelerated test results are the data which will be used to qualify structural components. So it's imperative that we start now in real time testing.

Some of that will come with actual prototype component testing, we realize, just as it did in the area of fatigue.

Let me summarize. In testing we see that our problem is not a simple one. We are very pragmatic in what we are doing here. We are approaching the problem with tools which are not well-tuned at this point. In the area of resin synthesis and quality control we are willing to use something less than design data generating test methods for design data.

But when design data is required, we must use tests which produce those data.

And finally, when we go into service qualification, our test methods must be accelerated but must also be related to real time behavior.

I think the floor is now open for discussion in this area.

MR. BORSTELL: I hope you all bear with me, because I am going to make a little speech which I think needs to be made at this meeting.

In the past 10 years, due to the considerable effort on the part of a large number of people, we have reached the point in composite structures where they have been used on a large number of airplanes. Today, industry and Government organizations are trying to qualify graphite/epoxy empennage structures for the B-1, F-16 and F-18 aircraft. Since 1968, we have had boron/epoxy stabilizers on the F-14 and F-15 aircraft, and there are probably 300 planes flying around with advanced composite stabilizers.

I think we have solved the manufacturing problems and reduced the raw material cost to affordable levels. Thus, the cost performance picture makes composites attractive.

Now, somebody has raised the critical issue of moisture in advanced composites, particularly graphite/epoxy. This issue also came up with boron/epoxy and we found that we did not have a problem. But, now we are again faced with this issue, and we must resolve it right now, because these new applications must be certified for production soon. Otherwise, the composite development effort may slow down drastically.

Much of the data comes from accelerated testing which does not reflect actual service environments. We must first determine if the accelerated exposure is causing the problem and how significant it really is. I think the biggest contribution that all of you people can make is to come up with

a test program that can be accomplished quickly to determine if there really is a problem.

I am not sure that under a realistic exposure a problem exists. From the theories presented today, I am sure that some minor cure process modifications would help improve the performance of saturated laminates and that might be enough.

Also, I think that moisture barrier coatings should be developed, particularly to seal the edges. Unfortunately, this topic has not been explored at this meeting.

At the same time, I say let's get some more talent to bear in the polymer industry to develop some improved resin systems. Because of processing restraints, we should stay with something that handles like epoxies. Let's get these new resins going and let's start characterizing them.

And, I feel that we should get some structure, saturate it with moisture in a realistic manner, and test it in elevated temperature fatigue. Also, let's dedicate some structure for life cycle testing.

But, I think these are all things that we have got to do now. If we don't do them now, we will lose the opportunity to use graphite/epoxy in near term aircraft and the aircraft will lose the performance pay offs that composites provide.

So, I think these are the kinds of things you ought to be looking at now.

DR. PIPES: Take the mike over there Bill.

MR. WALKER: I agree with you in certain aspects of what you say, sir, but I think the days of guts development programs and hardware development to get the systems is, I hope, in suspect by the Air Force, without paying proper attention to the adequate technology base before systems commitments by certain groups or individuals.

Besides the problem the Air Force has had in going with the graphite full depth thing called core zone tail service on the F-4, they began falling off in flight, because the honeycomb core corrodes away due to moisture getting in there.

The problem's got to be thought through, when you are faced with costs of ownership projection, and it's not simple enough to simply talk about real world environment. They vary all over the place, their manifestations in the failure processes, they are going to be different, and it's the goal of the program that we have tried to bring together here some talent to bear on that problem.

My feeling is, we got this problem today, we are going to be faced with the IV and UV problem tomorrow, and certainly I doubt whether the chicken wire and the electrical strips that I have seen for lightning strike protection - man, if I had to fly one of those things through a lightning storm, I'd have my rosary beads with me, I'll tell you.

Thank you.

DR. PIPES: Yes, Bill Jones.

MR. JONES: I'd like to compliment what Bill Walker indicated in his talk. There are some important things here. First, we recognize that there are going to be airplanes swishing overhead while we are busily working at our desk, and they will be flying with the things that we are working on, and that's great. Composite material systems will be put into service before long term durability questions are fully resolved.

Second, National priorities are currently changing. Instead of "higher and faster and hotter" as a major objective, it's "let's fly them longer and cheaper". And I think we can do a reasonable job with what we know now. But when we consider all the currently recognized phenomena, it is clear there is more work to do. Any progress will help make the next airplane last longer.

DR. PIPES: You are not the only person that's stated the point that you feel that if this problem isn't properly put to bed in the next two weeks, that they will cancel all composite utilization. I have heard that a couple of times. I heard that at the Battelle Meeting.

This community that we have brought together here is not addressing that problem, and whether or not we should, I am not sure. But the scientific community is not being brought together to solve an immediate design problem today. It's being brought together to talk about what are the problems we need to solve to make sure this material system is utilized

properly in the future on a continuous basis. And if you need some of these people to be working on the immediate problems to help you solve them, then our meeting probably has served a dual purpose in making them aware that there are some immediate problems that need to be solved which have probably some uneconomical fixes or some crude fixes that they can participate in, and I encourage them to do that and I encourage you to interact with them and use them as best they can.

But there is a product problem here and it is a long-term problem. It is that problem that we really have been convened to entertain.

Tom?

MR. BENNETT: Yes, I'm Tom Bennett, ASD, at Wright-Patterson Air Force Base.

I think what we are drawing out from different people here is a time phasing problem that we are most definitely faced with.

I think that we have been very enthusiastic in pushing composites into some of the aircraft we have now. We are trying to develop procedures to qualify them. We are having to become very serious about what it takes to qualify and/or certify these articles. And I think this has made the Air Force realize that we don't have the data base that we actually need to be able to intelligently specify qualification and certification procedures that would allow us to in fact guarantee, or at least have some sort of feeling for,

what is going to happen to these parts twenty years from now.

The Air Force has undergone a very tedious and a very painful reexamination of what they have been doing for the last few years, and we are in the process of reorienting. I think that we are going to have a lot more emphasis on gathering the data base that we need. This meeting has opened my eyes a lot, because if nothing else, it's made me fully aware of the gap between what the people doing the R & D work feel our problems are, and what we feel our problems are. Because, quite simply, we have some real pieces and parts flying. We have had some real failures. We are not beginning at ground zero and saying, "If we could start all over with a clean piece of paper - ". We have quite a few parts flying now, some have been out five to ten years, and we are getting failures back. We are getting failure mechanisms. And we would be more than pleased if we could only begin to understand what has happened to us up to this time, and what we can do about it to avoid the things that are already happening to us.

I think this is important and I like to hear people talk about a moisture resistant matrix. But to us in the here and now business, we have to realize that any time you come up with a completely new matrix material, we will have to have several years of qualification and background just to duplicate the data we have on the materials we now use. In spite of what Max seems to think about taking six to nine

months, he can design the part, but I'm sure that we would have to go through quite a laborious procedure to requalify whatever new matrix material he came up with, particularly if we had already qualified the parts that we have available.

So we are going to welcome any R & D help we can get.

I don't want to sound like some of us have. I don't feel the same sense of emergency. With all due respect, we have B-1's flying with metal tails right now and could in an emergency continue to do so. We do want to get all the information we can about composites because I think for the next generation of airplanes and very possibly for replacement parts for the airplanes we have got flying now, it could be very important for us to have all the benefits that the composites will offer. But we have to know what we are doing.

I think someone else alluded to the fact that we are in a different environment. A few years back we could say, "If it gives us an ounce of performance, I will give you many million dollars to go do that." Right now we don't have the many million dollars. Our ability to accept additional procurement cost is just not here any more, and to accept any additional risk right now might jeopardize an entire system.

So we have to be very careful what we do. And that is particularly true in light of the fact that there are no real requirements right now, particularly in the air frame structure, that says you cannot do it with metal. Although it may not be the best way to go, it's one we feel a little

more comfortable with right now.

So I think the burden of proof is on the composites community. We do want to encourage everything we can so that we can take advantage of composites, but we can't afford to be stampeded into something just because it is a new technology.

Thank you.

DR. PIPES: Irv Wolock in the back. Can you get him the microphone?

DR. WOLOCK: Wolock, Naval Research Laboratory.

Byron, I hate to change the subject and bust this up, but I'd like to get back to three points that you have made.

One, you say that you question the need for doing tests on resin properties because you weren't sure that you could translate those into composite properties.

DR. PIPES: That's right.

DR. WOLOCK: In that case, I think Walt Rosen has been misleading us, and I would certainly think that is something that if we had more time we could discuss, but I don't think a lot of people believe that.

DR. PIPES: No. I think that is a controversial topic. It turned out that our group didn't feel very strongly about that. The producers feel that they need to make neat resin tests because the end users in some cases want that kind of

test. But there wasn't anyone in our discussion who felt that they could take neat resin properties and predict the composite properties any more than they could take bulk adhesive properties and predict what is happening in an adhesive joint. The two problems are in fact analogous, and the statement that we made was, if one can do it with a composite, why do it with the neat resin system? Is there a driving force for working with the neat resin system when in fact a small step takes you into a composite system, and in that system you know the properties that you are measuring are composite properties.

DR. WOLOCK: Well, I'm at a loss for words. Good Lord, if you are playing around with new resin systems there is a big difference between running some tests on that resin and developing a method for producing a good laminate with that resin. We have had some work going on in our chemistry division at NRL and they have come up with a lot of new resin systems.

Now, if every time they change that resin they have got to come up with a new method for determining the proper conditions for molding that thing, the costs would be tremendous.

So really the stiffness, the tensile properties, the elongation, the water absorption, you can tell a lot by running a water absorption on a neat resin sample as opposed to making a composite. It sure is going to give you a good idea.

But anyhow, I guess the point is I don't agree with that.

Let me go on to the next one.

DR. PIPES: I think you are right. That's a controversial point. And that just happens to be my own personal position.

DR. WOLOCK: The second point is, you are talking about a standard condition for testing, and of course we have been led to believe that ASTM was gospel, and they say condition at 23 C and 50 per cent RH, that's great. But then Joe Augl tells us, if you have got a certain size laminate and you have exposed it to those conditions for forty-eight hours, you will have one moisture content in a certain gradient, whereas if you have it at those conditions for two weeks, you have got a different moisture content.

So that is no good any more because it's been dated to show that your properties are affected by that.

And George Lubin has suggested going back to a dried condition and of course you have to determine what that means now. But that sounds like a good idea.

You have talked about uniform moisture profile, and of course that's pretty damn tough. You surely don't mean saturation, because again Joe says for a thick laminate that could be about fifteen years.

DR. PIPES: It could mean you test thin laminates only.

DR. WOLOCK: That's all right, except sometimes you are interested in thicker laminates and you want to know the properties of some of these thicker laminates too.

So I don't think you can, you know - let me put it this way. I don't think your committee can say, "We are going to constrain you to testing one-eighth inch thick laminates," because that is not going to -

DR. PIPES: I think the point I was going to make is that you are right. ASTM methods don't exist. The ones that do exist have to be reexamined, we are not satisfied with them. But we'd like to see some standardization around the country so that when we see data we can compare some of it. That's basically what we are saying.

DR. WOLOCK: I will throw out George Lubin's suggestion of trying to work back to a dried state, and we will drop that, and I will go on to my last point and sit down.

And that was with regard to joints. You said that adhesive joint data should just look like resin dominated properties. I think that is what you said.

DR. PIPES: I said that in fact that could happen.

DR. WOLOCK: Yes, but that's fine if your failure is in your resin, is in your -

DR. PIPES: Adhesive.

DR. WOLOCK: -adhesive. But you may find that especially

in moist conditions that you might throw the failure back into your interface, in which case it's not so and it's not infeasible, unfeasible - well, one or the other - that your moisture is going to - could certainly change your mode of failure from the adhesive to the interface, in which case it's not so, you really have to test it.

DR. PIPES: I think that's true. If you don't move the failure from the adhesive into the adherend, then you are failing in a mode which is resin-dominated in the composite.

Renton had a question, Jim Renton.

DR. RENTON: Jim Renton, Advanced Technology Center.

Two points I'd like to make, one based on what I have heard up to this point. There are a lot of loose ends, and the polymer chemists are doing one thing and the mechanics people are doing another. I would just like to make a recommendation that you give serious consideration to encourage teams like the polymer chemists and mechanicians to work together so they will know what each other is doing instead of trying to get it out of a technical paper and wonder, "Well, did he condition it this way, did he do this, did he do that?"

If they can bring themselves to work together maybe they can solve the total problem instead of bits and pieces and it would be appreciated much more.

Second, I have heard conflicting evidence, and I bring this up because we do have some very notable visco-elasticians in the room; is it of necessity to bring visco-

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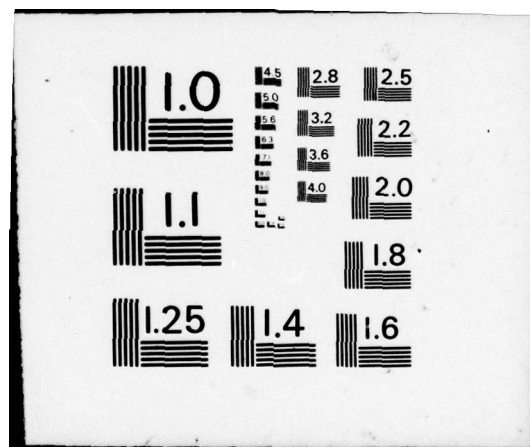
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elastic analysis into the moisture temperature problem of composites when we are trying to analyze it, or is it just necessary for the matrix-dominated mode? Does the shift factor that takes place in adhesives and resins really come into being?

Can we use things like the shift factor? But basically is the whole idea of viscoelasticity necessary?

I hope someone -

DR. PIPES: I think there was some statement made earlier about the time dependent properties, implying viscoelastic behavior.

DR. RENTON: How about the importance? Is it or isn't it?

DR. PIPES: How important is very difficult to assess.

DR. SCHAPERY: I'm generally suspicious if I see a modulus decrease with increase in moisture and temperature, regardless of the fiber direction. I suspect that viscoelastic phenomenon represent a large part of that decrease. You might be able to justify as an approximation some sort of a quasi-elastic analysis; but you have to be very careful about the conditions under which that will work. But I certainly look at moisture, and temperature effects, if increases cause a reduction in modulus, as really going hand in hand with viscoelasticity.

The modulus just doesn't decrease because of only

elastic phenonena.

DR. PIPES: But not necessarily linear viscoelasticity.

DR. SCHAPERY: Yes.

DR. LEVY: Ram Levy, McDonnell-Douglas.

I'd like to take advantage of that unique opportunity. The discussion was sliding to more basic, more of a strategy type of discussion. I wanted to interject some comments before we switch to specifics, and I have made one observation in that one particular topic seems to have been neglected in all these discussions, and that is the topic of moisture barriers, effective moisture barriers.

In my opinion, nobody wants to attack that subject mainly because nobody, I think, has the knowledge, or doesn't have any good ideas that would be - could effectively counteract criticism from outside and so on. And the reason for that, in my opinion, is that the scientific talent that reflects the people that are here does not include the type of people that might come with innovation in that particular area.

In other words, what I am saying is we have to draw on scientific talent in the chemical community and the chemical industry, which is usually outside of this area of the space type of structures and polymer chemists and so on.

Of course, polymer chemists that are doing the synthetic part, I don't know how many synthetic polymer chemists we have represented here, but the reason for, the main reason

that we ought to think about moisture barriers, is just because of the reasons that have been mentioned here, because of the inertia that builds up into developing a resin system, the technology builds in a period of several years and now if you are looking into new resin systems, you have to start the whole cycle all over again.

However, if you effectively develop a moisture barrier, you can retain that technology base that has been accumulated so far and just work on the barrier.

In other words, you can use everything up to that point and develop the protective coatings.

And I also want to know how much work has been done on that area. Are there many groups working in this throughout the country? We have heard here and there about some attempts. I know that there have been a few attempts made in McDonnell-Douglas, but they have been abandoned maybe due to lack of good ideas or maybe just because they run into blind alleys.

And I would like to ask the people in the Air Force if they know of anybody that is actively pursuing that or are they funding research along these areas?

Thank you.

DR. PIPES: Joe Augl seems to have an answer.

DR. AUGL: You can get moisture barriers. The best I would recommend are thin metal coatings or foils. If you can bond it to the composite, that would do the job. Organic moisture barriers do not prevent diffusion but will only

reduce the rate at best. We have calculated just a few of the systems. Since the thickness of the coating is restricted, you have to have an extremely low diffusion coefficient for the coating to effectively prevent moisture from penetrating within the time frame of interest.

So I think organic coatings are not very suitable, where moisture barriers are concerned; though with Teflon, polyvinylidene chloride or polyvinylidene fluoride you may reduce the rate of moisture penetration to .6 or at best to .4 (taking the relative rate 1. for the uncoated composite), simply because of the limitation in the coating thickness you may apply.

There are other benefits, of course, that the coating will give you. It will protect you from ultraviolet radiation, and also, as N.A.D.C. has shown with their outdoor exposures at Panama on panels with and without coatings, that coating is definitely beneficial in reducing the irreversible degradation. Though, it does not prevent moisture from penetrating.

DR. PIPES: There is another comment back here. There should be a mike right over there.

DR. BASCOM: Bascom, NRL. The question was raised whether anyone was working on coatings. Dr. Griffith at the Naval Research Laboratory has synthesized fluoroepoxy resins which appear to have some benefit as moisture barriers; but as Joe points out, you cannot use an organic coating to prevent water entry. You can only slow it down.

There is another benefit from the fluoroepoxys in that they are easily cleaned surfaces. They are now being used as paints on aircraft to reduce maintenance time and costs.

MR. WALKER: Bill Walker.

Byron, your discussion about service qualification testing and methodologies where you referred to the need for real time, load temperature-moisture tests for comparison with the accelerated test, if you hypothesize at this point that the Air Force position in future hardware is going to be real time, moisture and temperature, you don't have to be very bright to figure out that's going to cost a lot of money. I think it can have a big impact if at this point you ask yourself, "Hey, is there some way, using our smarts, we can, you know, accomplish the goal of interrogating the failure modes of structure through some other means?"

I don't know what that would be, but I think it's a properly addressed question to a research community such as we have got here, because the impact can be tremendous if we can find some other way to simulate all this stuff.

DR. PIPES: We can certainly take a bounding approach, and take the worst possible case, and use that as an accelerated test condition. But it certainly means that your systems are significantly overdesigned, and that is obviously what we will have to do, I think.

I'd like to turn it back over to Dr. Daugherty.

DR. DAUGHERTY: Thank you, Byron. Moving on to Group 5, the group leader for the Nondestructive Evaluation group is Mike Buckley from the Air Force Materials Lab.

5. Nondestructive Evaluation

DR. BUCKLEY: Thank you. Let me say, first of all, I'm a substitute for a substitute spokesman for this group. The main contribution I have to make is some criticisms about this group and the way it's going about its job.

Now, it seems to me that the utilization of composite structures is going to be driven by cost. And what is going to drive that cost to a large degree is inspection. You are not making perfect materials, and they are going to have to be inspected no matter what their quality.

In general, the people with the expertise on how to make composites don't talk to people who try to inspect them. As usual, we go along in our own little worlds. You have built up a big community here, worrying about the technology of composites and almost nothing on how to inspect them.

You are asking the inspection people to answer the most difficult question, i.e. what is the anticipated service life of a component for its anticipated usage? So that you want a crystal ball. In the long run, proof-testing is probably not a viable option for insuring structural integrity due to its high cost and intrinsic difficulty.

Where are we today in inspecting composite structures? We have shown no feasibility whatsoever to non-destructively

predict serviceability. The best work, in my opinion, is Dave Kaebel's, research on moisture detection; primarily because he synthesized the problem of inspection with the problem of the materials and attacked it from an overall viewpoint.

However, we don't have the supporting data we need. We don't know what the modes of failures are, so that in general we don't know what we should be looking for. We are just starting to learn what, in fact can be measured non-destructively. We have only recently attracted the type of people to work in NDE necessary to make significant advances.

We have, I believe, several good approaches for the inspection of composites being funded. There are several more efforts which I believe should be funded, but this is still a small number.

What I am going to suggest, which I think our group felt would be worthwhile, is to propose that some organization undertake sponsorship of a rather long-term workshop, with something like ten to fifteen people for about a month, at a nice location - such as the Navy Post Graduate School.

If we are to develop a quantitative NDE capability for composites we are going to have to get people really working together in this area. This workshop would provide a start at exchanging information and stimulating each other.

So I think there is one other program that hasn't been mentioned, and I am not qualified to mention it, but the new composites reliability program (ALPO) out of the Materials Lab, which is planned to be on the order of 50 man-years,

may have a major impact on this area.

DR. PIPES: ALPO?

MR. BUCKLEY: ALPO. Dog Food.

This is on the order of 50 man-years level of effort, and maybe that's the kind of effort which is needed.

But somebody ought to attack this area and sit down with ten or fifteen people and lay out exactly what we do know and what our options are and try to develop people with this interdisciplinary expertise.

I believe it's needed and without it we are going to be limited in the progress we can make. The O&M costs in DOD are rising rapidly. They may preclude using this class of materials.

Bill?

MR. WALKER: Michael, I agree with you, but I think you begged the issue.

MR. BUCKLEY: We did. I admit it. But I have to also answer - you will notice we had five people in our group and you notice how many you had in the other groups.

MR. WALKER: There is a message in what Mike's covered, that there is the need to integrate that end, again, and look at the life cycle costs and where this whole technology is going. It's essential. It's unclear in view of these environmental effects and what is going on in the polymer

chemistry in this area, what techniques we can use among the tools that are currently being applied to metals and ceramics and some of these other things.

And I think that there is a lot that needs to be done in this area, and I'd certainly like to see something - the Asilomar program next August at the Rockville Science Center program, where you have the large NDE community addressing them in this particular problem area with some good ideas, because I think it needs some good ideas.

DR. BUCKLEY: Let me just comment on that, Bill, because you threw it back to me. I think we need more time, since we are talking about a broader area out at Asilomar. We really need a good period of time to really sit down and work this. This is two days. Many people in a more established area said we could talk for weeks.

I grant you we will have the NDE people at Asilomer, but they won't have time to learn about the composite materials. We really need another meeting specializing in NDE of composite materials. I calculate that it will cost you, Bill, about 40K to 50K, but I think it would be worth it. I really do. You hopefully will end up with a good R & D plan, and have a few people who understand both sides of the house who can do something about it. We are not going to go it with short meetings, there is too much to learn.

DR. ROSEN: Can I ask you a naive question, Mike?

DR. BUCKLEY: Sure.

DR. ROSEN: I may have things wrong, but I see you here as a representative of AFML and you tell me they are going to have an advanced composite serviceability program with 50 man-years and then you say, "Hey, you guys, somebody out there ought to put together all these different people and study the technology".

Well, why don't you take one of the man-years off the fifty and do that?

DR. BUCKLEY: That hurts. I don't control that program, but I can yell at Bill Walker. So the people controlling that program apparently aren't here. I'm surprised, because that's a very big activity. It would seem appropriate to that program at that level of effort to do just what you said.

DR. SENDECKYJ: George Sendeckyj, Flight Dynamics Laboratory.

I'm slightly familiar with the ALPO program and it's based on the same things the NDE community has done to themselves. There was a meeting, a workshop, about two years ago at Wright Field and the NDE community told us, "We can do anything you want us to do. Just tell us what you are looking for."

And ALPO is a program that's designed to give them a chance to prove that they can do what they claim they can do, and also give us information on what we should be looking for.

DR. BUCKLEY: Let me just comment. Are you speaking of the NAMB Workshop in Dayton a couple of years ago?

DR. SENDECKYJ: Yes.

DR. BUCKLEY: That was generally considered less than successful.

DR. SENDECKYJ: Yes.

DR. BUCKLEY: Because of every corporation you ask, "Can you inspect composite structures," they will say, "Yes, we can find anything we are required to find."

That is true, because the only thing you ask them to find, is if it is in one piece. You are not asking them to tell you the strength of it or its durability, but rather what you are asking them to find, they can find; and those are the answers which they got at the NAMB meeting, and part of it's corporate policy. Nobody who is bidding on an aircraft is going to say, "I can't inspect it."

MR. BENNETT: I think it's very refreshing to hear the NDI community coming out of Wright-Patterson talking about getting together, because I think that I agree with George. I have been told that it's not an NDI problem. We can identify a lot of defects but we can't establish which affect the structural behavior. I believe you are alluding to the fact that we have to start working together.

DR. BUCKLEY: You can't separate the two.

MR. BENNETT: I have been through quite a bit of the NDE work with this in-service evaluation of our composites and we can indeed find an awful lot of things in the parts. There is an awful big area where we can, in fact, apply our NDE methods currently used on metal and honeycomb to this type of structure. I think there are a few areas, such as NDE to detect moisture levels and moisture distribution, where we do actually need new work.

But we have to learn somehow what these defects mean. We have to sensibly establish the structural limits on the size of voids and other defects.

DR. BUCKLEY: Right.

DR. PIPES: That's not an NDE problem.

MR. BENNETT: I realize this, but I hear a new thing coming out of the NDE people that I haven't heard before; they were telling the whole community before, "You don't have an NDE problem." I can find more than you know what to do with now, and that is true.

DR. BUCKLEY: You have a two-fold problem. If you separate defects into categories and collect them by their severity, I don't care what type of defects they are, if we cannot resolve them into those particular categories with some inspection method, we have gotten nowhere.

Somehow this has to be tied together, and frankly, the problem we have is that structures people, the people who

want to build hardware and have all the money, say that, "We don't know that NDE cannot, in fact, do it" and therefore all they ever want to do is look at state of the art techniques, and they never really get the answers.

We are in a poor position right now. You accept the fact that the failure models are inadequate but you are not willing to believe that you can't inspect them. I don't understand why. If moisture is a problem, you know you can't inspect it.

DR. WOLF: Wolf, McDonnell-Douglas.

I think the testing comes after you decide what you are going to look for. You have to decide what mechanism to hit, then you find a way to look for them.

DR. BUCKLEY: I don't think you can do that independently is my point.

MR. BENNETT: How can you come up with a test to look for something when you don't know what you are looking for.

DR. BUCKLEY: Right, that's true.

MR. BENNETT: That's a tough job.

DR. BUCKLEY: That's right. And what is the sense in discriminating different modes of failure if in fact you have no method of ever measuring those different modes of failure?

MR. BENNETT: But what is the point of developing the

method if you don't know if they are detecting an important failure mechanism.

Once you find the failure mechanism, what the problem is, somebody will come up with a test for it.

DR. BUCKLEY: Not necessarily.

MR. BENNETT: I can give you an example. People bring in a composite, or pieces of it, I say, "What's in it?"

Well, now, that's not a fair question. Within what limits are you talking about? Parts per billion, parts per million? You just want the total epoxy or you want every constituent of the epoxy in there? You know, because the number of epoxies that are available must be, I don't know, a hundred thousand. Any chemist, as fast as you can write them, you can put another oxygen on there, put another carbon on there, put an OH on there, put an F on there, man, we've got more.

So, when you bring the composite in, maybe the specific chemical formula is causing the problem. After we decide what the problem is, somebody can come up with a pretty good test for it.

DR. BUCKLEY: That's right. The point - let me just comment on this - you get the same problem in metals. You look at fracture mechanics -

MR. BENNETT: It's easier in metals.

DR. BUCKLEY: That's right, a much easier problem in metals.

Well, I would question that, even within the bounds of fracture mechanics, if you look at what we inspect for today and what you need to make any sort of accurate fracture mechanics calculation, there is little correlation.

DR. PIPES: That is not true.

DR. BUCKLEY: That is true to a very large degree. You assume a crack, number one, you do not require your inspection to give you the shape of the defect. If you look at the variation of that on a fracture mechanics model, it's tremendous. The only alternative you have is to overdesign and be very conservative and that is dollars and that is what is pushing the system again.

So you are paying a very big price for this lack of a quantitative inspection capability and you are much worse off in this composite business. If you are going to sit around and wait for detailed knowledge of failure modes, which are going to change because we are going to learn more as those systems get older, you are going to have to get an awful lot smarter generically in this field, an awful lot smarter to interact with these modes of failure.

I'm just saying it's interacting. We sit back, "Okay, you guys have now answered the total question as to the modes of failure for any composite structure in any environment, and now you will tell me that all I have got to do is measure the

modulus." Okay. And I'm all done. If that is true, great.

In the meantime, you are not going to get that stuff out in the field because no one has shown that they can measure it. It's not going to be simple, it's going to depend on the environment. You are going to change the criteria, and unless you are going to get some lead time, you are going to have the same problem you are running into in everything else. We haven't invested in the scientific foundation of NDE.

DR. WOLF: For example, like the NARMCO 5208 resin. You say, "Well, sometimes the batch just doesn't cure properly. Why?"

Well, you can take it apart as a chemist and you can find all kinds of things in there. One of the problems you have, they won't even tell us what's in it, so we have to take it apart. Maybe anybody that's a chemist knows, sometimes it's part per million that drastically affects a reaction and we can come up with a test for just about a part per million of any element of any compound you want. But we have got to know which one you are looking for, and if you just take a resin a priori and say, "I want to look into parts per million," they will laugh at you. Nobody would do that because that's an unbelievable job.

You have to find out what the problems are; what are you looking for.

DR. BUCKLEY: Okay.

DR. WOLF: Then you will get the tests.

DR. BUCKLEY: I have to try to get the last word, we know that there are certain types of problems unique to composites at least as compared to metals, moisture being an example of that type of problem. This may influence the strength and can lead to premature failure. We should be looking at methods to non-destructively determine moisture, okay.

Whether you know explicitly how moisture relates to what service life, we also have to learn how to find defects in an inhomogeneous material. We know that cracks will cause failure. What size may vary.

But, again, simply from a cost viewpoint, you have to be selective, and these are new materials to work in and these should be parallel developments. You aren't going to all of a sudden discover entirely new phenomena, most likely, which you are going to have to worry about.

What you will get better at is in telling me what levels of moisture, what size defects, where they are located, etc., and how severe they are, which is really the accept-reject criteria.

We now know generally what type of things to look for and we should be looking at them and we should be interacting much more on what is already known about them from laboratory work.

MR. JONES: Mike, I'd like to amplify one item that you touched on and I'd like to point out its value.

In the situation where we are trying to communicate between two disciplines, each and every channel of communication turns out to be very valuable. In adhesive joints and in metals it turns out that fracture mechanics is indeed one of these channels of communications. It's kind of a narrow and width, and there are some unknowns, particularly in the applications to composites and adhesive joints. Some of these unknowns are being treated in the "Effects of Defects" program that George Husman is monitoring at McDonnell-Douglas.

Yes. There are some unknowns in those programs. Yes. There are some limitations in fracture mechanics approach. Yet there is still value, (certainly in the communications channels that are opened) in relating structural degradation with observable and measurable features such as cracks.

In composites, the relations are not yet clear. There are cracks being observed, but there are discontinuous growths of those cracks. So right now that's even a narrower band width.

But I'd like to encourage that we at least recognize the value of these channels. Thank you.

DR. BUCKLEY: Thank you.

DR. SENDECKYJ: George Sendekyj, Flight Dynamics Lab.

People do recognize the usefulness of NDE. I know that Paul Rose in his new program for NASA, Langley, where they are following experiments, are very careful with NDE

techniques. We are doing some in-house work, both laboratories, and that is how we are learning what has been the state of the art of NDE methods. They just can't tell us what we want to know, or it's too much of a nuisance to use them.

DR. BUCKLEY: I think that's my whole point.

But now the cost figures are coming up. People propose proof testing as a solution. It looks very expensive and we are not so sure how well we can proof test. You are asking something of inspection, which is far above what we presently do for metallic structures, and we are not that good on metallic structures. So there is no question that you are going to have to invest in this field. There is no question the people who work in it have to understand this kind of a system, and I am saying we have got to get these people together and build a group of experts who know the composite structure, know inspection, and are just smart people.

MR. WHITESIDE: Jim Whiteside, Grumman.

You keep referring to these costs that are going out of sight. I have been going through the development of full scale structure with composites for about eight years now. We have finally got to the point where we are talking about justifying structures on the basis of cost savings. My management has been following this kind of thing pretty carefully, and I'd really like to know what you are talking about.

DR. BUCKLEY: Okay.

Bill is dying to answer that one. Bill Walker.

MR. WALKER: The kind of costs we are talking about is the whole bag of costs, not just cost to get it out the front door when you sell it to the Air Force.

MR. WHITESIDE: Projected life cycle costs?

MR. WALKER: That's what we are talking about, projected life cycle costs.

MR. WHITESIDE: Who is making the projections?

MR. WALKER: I don't know that it's really published anywhere. I know it's the general consensus that we are staring at a problem area in terms of cost uncertainties, simply in production and manufacturing costs, and then you add on to that uncertainties in life cycle costs and the experience that Mike's talking about from the data coming back in on some of the composite parts that are in service, like in service failure of the F-4 rudders, and as far as the research community saying, you know, "We have got a problem here in the NDE business. We might as well recognize it in conjunction with the rest of it and get on with it."

DR. BUCKLEY: Bill, perhaps I can comment on those costs a little bit.

Maintenance today, the operating and maintenance budget of the Air Force is probably the fastest rising budget. We can cut down the R & D, we can't cut down the cost of

maintaining the Air Force.

We have got a very complicated system of maintenance. About 24 per cent of the Air Force personnel are involved in maintenance.

MR. WHITESIDE: I'm aware of this, but it's these projections you are talking about.

DR. BUCKLEY: Well, it's very simple. If that composite structure is going to require special certification, like a proof test, you can look at the cost of a proof test and it's very, very expensive.

MR. WHITESIDE: McCarthy concluded that proof tests on the B-52 aluminum wing skins would have been a lot cheaper than the inspection in repairing all those holes.

DR. BUCKLEY: It's going to depend a lot on the structure. It may be a lot cheaper to replace that composite structure with a piece of aluminum, which you in fact can inspect. You can look at the cost figures of one recent aircraft, which I have, but I don't have them with me, the cost of that proof test is unbelievable compared to other aircraft.

Then they are still taking the airplane apart to inspect it anyway. This is an additional cost.

DR. PIPES: That proof test was required by design error.

DR. BUCKLEY: We have not learned how to make zero

design errors and we probably will continue to.

DR. PIPES: Material selection.

DR. BUCKLEY: Material selection. Well, poor quality assurance is one.

DR. PIPES: Same thing.

DR. BUCKLEY: During manufacturing, the aircraft that crashed was inspected about twelve times. That defect should have been found. It was the state of the art. It wasn't a small defect by any means. The carry-through box had a crack about an inch and a half long. It wasn't found. The airplane crashed. The recovery program cost the Air Force a considerable amount to figure out what went wrong, and a very elaborate proof test was done, because it was inaccessible at that point once it's in the airplane for inspection. People are not willing to tolerate, I think, those sort of mistakes again. We have got to get a lot smarter about inspecting them and insuring their quality. It's a fact of life.

DR. DAUGHERTY: If we could come back at 3:45.

(BRIEF RECESS)

DR. DAUGHERTY: I assume that most people are back, so if we can get started. Because of travel arrangement considerations, the panel discussion will not take place. Dr. Vinson would like to say a few words.

DR. VINSON: There will be transactions of this meeting which we will get out to you some time, let's say, during the summer, as Byron said earlier, and we will be editing this or pre-editing it and therefore, for those of you who made formal presentations and reports associated with the study groups, we will send out to you our pre-edited review of your formal statements, and therefore you will have a chance to make any corrections. Obviously, some remarks will be edited or at least scrambled. I would like on this opportunity, to thank our court reporter, Barbara Johnson, for the tremendous work that she has done, and also I would like to formally thank our three student assistants, Bob Wetherhold, Nick Ballintyn, and David Adkins. They worked very hard. I will turn this back over to Bill Walker who will wrap-up the Workshop.

G. Closing Remarks

MR. WALKER: Thanks, Jack.

I'd like to thank everybody for contributing to the success we have had, and I'd like to make a few comments.

First off, to the last session, in case somebody misunderstood, Mike and I are always trying to sell things

back and forth to each other, so you have to understand those remarks.

In view of some of the concerns and skepticisms in the NDE business, I'd like to recall the message that John Halpin started off with, that the current position coming out of the AFFDL survey is that the potential for composite materials as a primary structure is still there. I think that is a key area which is meaningful for the Air Force to work into its technology base. The problems we have seen aren't show stoppers, but we have just got to work on them to bring them to a full maturity.

I think what you have all been subjected to here for the last two days is the OSR version of Ed Wu's Chinese torture. I can't believe how quiet Ed has been for the last two days. He really raised hell out of things at the NDE workshops a few years ago. That was referred to earlier.

But I thank you all for being so patient and contributive here, and in looking back at the objective we started with, which was to promote the interaction between two groups: polymer science and structural mechanics. I think we have done that. But interestingly enough, I think we have accomplished one other thing, and that is to promote some interaction within each one of these groups that I have seen here, which I think is also significant.

We also set out to identify the issues and research areas in the five areas or five discussion groups that were looked at, and that happened today, which has been a brain-

storming activity. That's how you can look at it. Because as Mike pointed out, you know what we need in the NDE group is to put a group together for a month and I'm sure in each one of the five areas you could vote a full three or four day symposium to these; but, you know, like the multiply choice test, you go through this thing and your first ideas are somehow probably your best ones.

That's the way we went through this the first time, which brings you to the problem of we started something, we got the ball rolling, what will you do for an encore? How is the best way to proceed from here, again in an interactive group.

Dr. Renton talked about earlier the idea of a team activity in certain areas. I'm open for some ideas in that, and, you know, if you want to form an informal kind of committee, we have another symposium, and if we have all got another meeting to travel to, and do we meet every six months or eighteen months, I don't know. I'd like some feedback on that.

What the next step is to enhance the interactive process, which I think the consensus of the group is in terms of the interactive experience, it's been stimulating.

One thing that kind of scares me, and I am sure it will scare Don, is that the mail for the next three weeks is going to have nothing but proposals in it. Thank God for 7-T at this point, because no new work can start in 7-T, gentlemen, so don't go home and start typing the proposals yet, because nothing's going to happen until the 1st of

October, and we are going to put this whole thing in perspective before then; and somehow I think it's our obligation, in this encore idea, to ask the Air Force Office of Scientific Research, to ask that Dr. Lehmann, the manager of Research for the Air Force, get back to the community with our research plans in this area, as to what our research programs in this area look like.

When and in what form that's going to take, I'm not sure, but I think that's the obligation we have to you at this point.

And that, I think, wraps it up from my point of view. I'd like to entertain any comments or discussions that anybody might have.

Don, would you like to add anything? Have I omitted anything?

DR. ULRICH: No, you have done very well.

DR. DHINGRA: Ashok Dhingra, DuPont.

I have been a good listener and have tried to understand some of the problems of the resin matrix composite in moisture, ultraviolet degradation, lightning strike, high temperature degradation, joining, inspection, etc. What I would like to suggest is that we take a fresh look at the metal matrix composite system. This has nothing to do with the fact that I'm a mechanical engineer/metallurgist by training and have been working in the metal matrix composite

area for the past few years, but I think some of the problems which have been mentioned, especially in moisture, high temperature degradation, lightning strike, corrosion and joining can be circumvented by using metal matrix composites.

Thank you.

MR. WALKER: Well, I certainly agree, and I know and I am sure you are aware of workshops that were conducted last summer and in the fall by Dr. Ellis Foster of I.D.A., for the metal matrix business. In fact, Dr. Foster is scheduled to come into OSR the week of the 14th, and present the results of his findings.

There are programs at OSR that are investigating the metal matrix business. Ed Vanreuth of ARPA is committed to a program in the metal matrix business.

The question here is not a decision on a material base, of whether you ought to be in one or the other. We see our job in the research community to look at the Air Force's technology base and the materials systems that it sees as a potentiality to operate at ASD or give ASD the options for cost and performance reasons to exercise with the least technology base in the materials systems that the industrial contractors of this nation know something about.

And in looking at the materials systems we ask ourselves what are the research opportunities, what are the opportunities that the research community can contribute to these materials or contribute new things so we end up with a

whole new set of materials; and I don't think the point here is to play down metal matrix or DS eutectics or ceramics supported by fibers. We have talked about chopped fibers here.

But I think the issue has been raised, and particularly in the Air Force in this one, because we have had a large technology base funding program in this area. So I don't think it is our goal to play down the metal matrix or any other material system that's going to give us the opportunity to do our job.

And let me say that I am saying that not simply from an OSR point of view, but every time I pay my taxes.

Any other questions? Comments? I'd like some reaction.

DR. PIPES: I move we adjourn.

DR. WALKER: Do I hear a second to the motion to adjourn?

(Motion seconded; meeting adjourned.)

SUMMARY

This Workshop has provided a unique forum for researchers in polymer chemistry and structural mechanics to learn of and discuss the serious problems caused by the deleterious effects of combined high temperature and high humidity on polymer matrix composite materials. The results of these discussions and the ideas of various researchers to solve or diminish these problems are given in Section F, herein, where each of the following topic areas is discussed in detail:

1. Physical Property Correlation Models
2. Characterization of Constitutive Properties
3. Failure Processes
4. Test Methods and Experimental Research
5. Nondestructive Evaluation

The reader, through studying that section, can identify the specific problem areas and approaches suggested by the participants to alleviate these effects, and can determine how he may contribute to the solution of the "hygrothermal" problem of polymer matrix composite materials.

THE EFFECTS OF RELATIVE HUMIDITY
AND TEMPERATURE ON COMPOSITE STRUCTURES

March 30-31, 1976

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